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NANOCOMPOSITES OF POLYMERS WITH LAYERED INORGANIC NANOFILLERS: ANTIMICROBIAL ACTIVITY, THERMO-MECHANICAL PROPERTIES, MORPHOLOGY, AND DISPERSION

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ABSTRACT

In the first part of the thesis, polyethylene/layered silicate nanocomposites that exhibit an antimicrobial activity were synthesized and studied. Their antimicrobial activity was designed to originate from non-leaching, novel cationic modifiers –amine-based surfactants– used as the organic-modification of the fillers. Specifically, PE/organically-modified montmorillonite (mmt) nanocomposites were prepared via melt-processing, and simultaneous dispersion and antimicrobial activity was designed by proper choice of the fillers’ organic modification. The antimicrobial activity was measured against three micotoxinogen fungal strains (*Penicillium roqueforti* and *claviforme*, and *Fusarium graminearum*). Various mmt-based organofillers, which only differ in the type or amount of their organic modification, were used to exemplify how these surfactants can be designed to render antifungal activity to the fillers themselves and the respective nanocomposites. A comparative discussion of the growth of fungi on unfilled PE and nanocomposite PE films is used to demonstrate how the antimicrobial efficacy is dictated by the surfactant chemistry and, further, how the nanocomposites' inhibitory activity compares to that of the organo-fillers and the surfactants. An attempt to improve the thermomechanical reinforcement of PE/mmt nanocomposites while maintaining their antimicrobial activity, was also carried out by combining two different organically modified montmorillonites. However, a uniform microscopic dispersion could not be achieved through this approach.

In the second part of this thesis, a number of fundamental studies relating to structure-property relations in nanocomposites were carried out, towards unveiling
strategies that can concurrently optimize selected properties of polymers by the addition of nanofillers. Specifically, the dispersion-crystallinity-reinforcement relations in HDPE/mmt nanocomposites was investigated. The influence of a functional HDPE compatibilizer’s characteristics to the thermo-mechanical properties of their nanocomposites was systematically explored. The appropriate compatibilizer, based on HDPE-g-MA, was identified from achieving the best mechanical performance, i.e., maximizing the tensile modulus improvement without sacrificing the polymer ductility, which was found to be achieved where the smallest crystallinity change occurred. It was revealed that lower-than-the matrix molecular weight HDPE-g-MA better enhanced the tensile properties across three HDPEs, compared to that of high viscosity HDPE-g-MA, while the flexural properties were not markedly affected by this parameter, but rather were mostly determined by the amount of clay nanofiller. Finally, polymer/layered double hydroxide (LDH, positively-charged layered clays, also termed as ‘anionic’ clays referring to their anion exchange capacity) were characterized as potential fillers for a variety of polymer matrices. The main focus in this part of the research was on the morphology and dispersion of the LDH as it related to their composition and their organic modification in relation to the nature of various polymers. Exemplary polymer matrices that span the range from non-polar to polar interactions –including Polypropylene (PP), polyethylenes (PE, and PE-copolymers), polymethyl-methacrylate (PMMA), polystyrene (PS)– were explored. It was observed that the LDH composition, organic modification, and polymer types were the parameters which controlled the LDH structure and dispersion, albeit in a rather involved fashion.
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It is with the utmost love and gratitude that I dedicate my dissertation to my family. I would not be this far without their support.
Chapter 1

Introduction

Polymer nanocomposites are currently heavily investigated, because of possible enhancements in mechanical and thermomechanical performance, barrier properties, environmentally-friendly flame-retardant character, as well as new functionalities, such as peelable heat-sealing performance and antimicrobial activity [1, 2]. One of the most attractive advantages, compared to the neat polymers and conventional composites, of using nanoparticles as fillers in polymers, is that the properties of the polymer matrix can be markedly improved at very low filler content. These improvements are generally associated to high surface area combined with high aspect ratio of nano-scale fillers [3, 4].

Traditionally, layered silicates (LS), such as talc and mica, have been proposed as the reinforcing fillers in polymeric materials for quite a long period of time [5]. After a major breakthrough in polymer nanocomposite technology by the Toyota research group, who achieved a polyamide 6/organically modified layered silicate with a remarkable combination of high thermomechanical properties [6, 7], the organically modified layered silicates, especially those in the class of smectite clays, and in particular montmorillonite (mmt), exploded in research activity. This single material became the reason to revitalize clays as functional fillers in numerous fields and applications of polymer composites, coining the term ‘nanocomposites’ as a new class of materials.
More recently, other types of layered nano-materials, like layered double hydroxides (LDHs) have drawn considerable attention in the same fields of research. LDHs may offer additional possibilities of applications, in comparison with cationic clays, because of their highly tunable properties and compatibility to a variety of polymeric materials [8]. Although LDHs are rare in nature, they are environmentally friendly, as well as relatively simple and inexpensive to synthesize in the laboratory and at industrial scales [9]. Examples of ‘new’ functionalities of LDH/polymer nanocomposites are: electrical property, luminescence property [10], photo/UV stability [11], antimicrobial activity [12]. One of the most promising applications being extensively investigated is the use of LDH nanofillers as potential environmentally-friendly (non-halogenated) fire retardant (FR) additives for polymers.

In this dissertation, the functionalities of the organically modified layered silicates (mmt) and their application in polymer nanocomposites were mainly explored. A novel property, their biological activity as an antifungal material, was systematically investigated for organo-mmt particles and their polyethylene (PE) nanocomposites. The optimization of polyethylene nanocomposite systems was further investigated by subsequently addressing the mechanical properties of these PE-based nanocomposites. Finally, the dispersion and morphology of organically modified layered double hydroxides in various polymers, such as poly(methylmethacrylate) (PMMA), polystyrene (PS), and PE were also studied.
Goals, Objectives, and Dissertation Structure

1. Evaluate the antifungal activity of selected free cationic surfactants and organically modified mmt against four fungal species and compare to the control system (without surfactant/organoclay).

2. Investigate an effect of surfactant dosage to the antifungal activity.

3. Prepare Polyethylene (LLDPE/LDPE blend) nanocomposite films incorporated with selected organically modified mmts promoting high antifungal activity and evaluate their antifungal efficiency compared to the unfilled polyethylene.

4. Identify appropriate functional (HDPE-g-MA) HDPE enhancing mechanical properties (emphasis on not sacrificing HDPE ductility) of HDPE/organo-mmt nanocomposites.

5. Prepare HDPE/organoclay blend nanocomposites and investigate the mechanical properties and their antifungal activity.

6. Investigate the property-processing dependencies by comparing tensile and flexural properties of selected HDPE/organo-mmt nanocomposites prepared via single step (injection molding) and two-step process (extrusion and injection molding).

7. Study the morphology and dispersion of LDHs in various polymers, including PMMA, PS, PE, and PP.

In Chapter 2, the 2:1 layered silicates (LS), layered double hydroxides (LDHs), and their polymer nanocomposites are briefly introduced. In addition, their chemical
composition, crystallographic structures, ion exchange reactions, synthesis routes, and morphologies are briefly described. These literature reviews are primarily focused on the materials used in this research.

In Chapter 3, a functionality of the selected organic modifiers (cationic surfactants) in organically-modified mmt (organoclays) as antifungal agents which are active against a broad range of fungal species, including soil- and food-borne organisms. Both free and tethered surfactants are used for a comparison in this systematic study. Additionally, the effect of dosage to the fungal growth inhibition is investigated across a broad range of concentrations.

In Chapter 4, the most effective organoclays (from Chapter 3), were incorporated into Polyethylene (LLDPE/LDPE blend) nanocomposites at organoclay content of 6% and 9% wt.%. Antifungal activity of these nanocomposite films is both qualitatively and quantitatively evaluated and compared to the control polyethylene film. Structural and mechanical characterizations were also carried out.

In Chapter 5, three different types of HDPE-g-MA based masterbatch systems (organoclay/HDPE-g-MA concentrates) are diluted by three different HDPEs at 0.2%, 0.5%, 1%, 3%, and 6% clay content. The thermal and mechanical properties of these nanocomposites are investigated and compared to the unfilled PE. Moreover, one selected HDPE/HDPE-g-MA combination is used to prepare nanocomposites by incorporating a mixture of two organoclays at a cumulative 6% clay content, and its mechanical properties and antifungal activity are investigated.

In Chapter 6, LDH/polymer nanocomposites were studied focusing only on the composite morphology and dispersion of organically modified LDHs (Mg-and Zn-based
LDHs) in various polymers, including PMMA, PS, PE, and PP. The influence of LDH compositions, and organic modifiers used to their morphology and dispersion is presented. Further studies of these composite materials (thermomechanical properties and fire performance) were done in collaboration with other groups and are not part of this thesis.

Chapter 7 depicts the conclusions of my dissertation and suggestions for future research work.
Chapter 2

Literature Review: Polymer Nanocomposites

2.1 Layered Materials

2.1.1 Layered Silicates

2.1.1.1 Structure

Layered silicates are commonly known as the cationic clay minerals. Among the most commonly used layered silicates, smectite clays, such as hectorite, montmorillonite (mmt), are naturally occurring 2:1 phyllosilicates. Their general formulas are presented in Table 2-1. Their crystal structure (Figure 2-1) consists of two-dimensional layers formed by fusing two silica tetrahedral sheets to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. The layer thickness is generally about 1 nm, and the lateral dimension of the layers may vary from a few hundred angstroms to a micron scale, depending on the source of clay minerals [13]. Parallel stacking of these layers leads to interlayer galleries, normally occupied by hydrated cations, which balance the charge deficiency that is generated by isomorphous substitution within the layers [14]. The degree of this substitution is expressed as cation exchange capacity (CEC), in terms of mequiv/100 g clay. This refers to total negative charges present from isomorphous substitution within the structure, the broken bond at edges, the external surfaces, and the dissociation of accessible hydroxyl groups [15].
Figure 2-1: The structure of 2:1 layered silicate [16].

Table 2-1: Formula and characteristics of smectite clays [13].

<table>
<thead>
<tr>
<th>Layered Silicate</th>
<th>Location of isomorphous substitution</th>
<th>Formula</th>
<th>CEC (mequiv/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hectorite</td>
<td>Octahedral</td>
<td>$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$</td>
<td>120</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>Octahedral</td>
<td>$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$</td>
<td>110</td>
</tr>
</tbody>
</table>

M=monovalent cation; x=degree of isomorphous substitution
2.1.1.2 Cation Exchange Reaction

Hydrophilic pristine mmt can be rendered to be organophilic via cation-exchange reaction of the pristine alkali cations with organic cationic surfactants, such as alkylammonium or alkylphosphonium [16]. This can promote the intercalation of organically-modified mmt by non-water-soluble polymers. The exchange reaction is generally expressed as follows:

\[ \text{RH}^+ + \text{M}^+ -\text{clay} \rightleftharpoons \text{RH}^+ -\text{clay} + \text{M}^+ \]

where \( R = \) organic group, and \( M^+ = \) exchangeable inorganic cation.

The cationic surfactants are bonded to the charged layers by electrostatic forces, while other noncoulombic forces may also contribute to this adsorption, in particular van der Waals attraction between the organic moieties and the clay surfaces, or the adjacent organic molecules themselves.

The interaction of the organic surfactants adsorbed in the clay layers was initially studied from X-ray diffraction (XRD) characterization by Lagaly [17, 18] and proposed to be dependent on packing density of layer surfaces, alkyl chain length, and temperature. The general arrangement of the chains between the layers was suggested to be “all trans” conformation forming either parallel to, or radiate away (called as paraffin-type) from clay surfaces with mono-, or bi-layer arrangement, Figure 2-2. The kink or “gauche” conformers, however, were observed only at high temperature conditions.
Further study was completed by Vaia et al. [19] using Fourier Transform Infrared Spectroscopy (FTIR) to characterize the interlayer structure of the alkyl chains. It was suggested that instead of “all trans” conformations, the manifold “gauche” conformations were generally intercalated along the clay surfaces, Figure 2-3. The arrangement of the chains may vary from liquid to solid like structure depending on alkyl chain length, packing density, and temperature. It was also proposed that all trans-conformers were found, specifically, when the cross-sectional area of the intercalated chains was about the same as the host area/guest molecules.

Figure 2-2: Alkyl chain arrangement within mica-type layered silicates: a) lateral monolayer, b) lateral bilayer, c) paraffin-type monolayer, and d) paraffin-type bilayer [19].
2.1.2 Layered Double Hydroxides (LDHs)

2.1.2.1 Structure

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds (HTlc), are classified as the anionic clays. The general formula of LDH is presented in Table 2-2, where $M^{2+}$ are divalent cations, such as Mg, Co, Ni, Cu, or Zn; $M^{3+}$ are trivalent cations, such as Al, Cr, Fe, V, or Ga, respectively; and $A$ is the interlayer anion of valence m. [20, 21]. The structure of LDHs can be illustrated in Figure 2-4 as a brucite like structure, Mg(OH)$_2$, of octahedral edge-shared layers in which some of the divalent cations have been replaced by trivalent ions giving positively charged sheets. These charges are balanced by intercalation of anions, such as nitrate, in the hydrated interlayer regions [22]. The interactions between the LDH layers derive from coulombic forces between the positively charged layers and the interlayer anions, as well as hydrogen
bonding between the hydroxyl groups of the layer with the anion and the water molecules in the interlayer [23].

The degree of isomorphous substitution within the layers is expressed as anion exchange capacity (AEC), in terms of mequiv/100g clay. The AEC varies as a function of the compositions and the types of cations as shown in Figure 2-5.

Figure 2-4: Structure of LDH [24].
Table 2-2: Formula and property of LDH.

<table>
<thead>
<tr>
<th>Layered Double Hydroxide (LDH)</th>
<th>Formula</th>
<th>AEC (mequiv/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[M$^{2+}_{1-x}$M$^{3+}_x$(OH)$<em>2$]$^{3+}$A$</em>{x/m}$ m$^{-}$·nH$_2$O</td>
<td>200-400</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2-5: The anion exchange capacity as a function of the amount of trivalent cations reported per formula weight [25].
2.1.2.2 Anion Exchange Reaction

Similar to that of cationic clays, the nature of the LDH layer surfaces can be changed by an exchange reaction with anionic molecules, for example carboxylates [26], sulfonates [27], or phosphonates [28]. The packing of the organic anions in the interlayer spaces crucially depends on the compatibility between the charge density of LDH layers and the charge/size of the intercalated anions [25, 29]. According to the choice of organic modifiers, a large variety of LDH/polymer systems can be tailored considering the highly tunable intralayer LDH composition.

2.2 Formation and Morphology of Polymer/Organoclay Nanocomposites

Depending on the compatibility of the polymer and the clay, three polymer hybrids are possibly formed, namely, conventionally phase separated, intercalated, and delaminated/exfoliated, as schematically shown in Figure 2-6.

Typically, the phase separated hybrids correspond to the conventionally filled polymers, in which the clay particles agglomerate, and lead to poor mechanical properties.

The intercalated hybrids are resulted from the insertion of extended polymer chains into the clay layers occurring in regular multi-layers with a repeat distance of a few nanometers.

The delaminated/exfoliated hybrids, in which the clay platelets (1 nm thick) are expected to be individually dispersed in the polymer matrix, result in high aspect ratio of about 1000 (fully dispersed) compared to that value of 10 found in phase separated
systems. The interlayer expansion of these delaminated/exfoliated hybrids is comparable to the radius of gyration of the polymers [3, 30].

![Layered silicate and Polymer](image)

Figure 2-6: Scheme of dispersion characters in polymer/clay nanocomposites: (a) phase separated, (b) intercalated, and (c) delaminated/exfoliated [1].

The structure and morphology of polymer nanocomposites are typically investigated by using X-ray diffraction (XRD) and Transmission microscopy (TEM). The XRD technique is the most commonly used method in order to get a fast qualitative description of the dispersion/structure of clays in polymer nanocomposites. It is used to observe the interlayer basal (001) diffraction, corresponding to the periodic stacking of clay layers; however, XRD can only trace parallel/periodic arrangements of layers, while
in case of disordered or delaminated/exfoliated structures, the (001) diffraction becomes featureless. In this case, therefore, XRD cannot give the complete information about the polymer nanocomposite structure.

The TEM investigation is a support technique used to get direct morphological pictures, as well as to provide information on the particles’ size and their dispersion, indicating the number of single layers in a multi-layer structure, and the distance between such layers, even for delaminated/exfoliated structures that do not show any XRD pattern. The limitations of this technique are difficulties in quantitative analysis, and sample preparation, and limited resolution only to the silicates positioned on the image edge-on [31].

For the phase separated systems, the clay tactoids still remain in the polymer matrix. The dark feature from TEM represents the clay layers and the brighter features correspond to polymer matrix, Figure 2-7. The X-ray diffractogram, thus, is expected to be the same as that scanned from the premixed-clay powder, i.e. there is no shifting of the 2θ, because of no platelet separation. In case of intercalated systems, the XRD scan shows the peak shift to lower angle, corresponding to larger galleries and spacing derived from intercalation of polymer chains to the clay layers. The clay layers (dark lines) are separated by the polymer and become parallel to each other. For completely delaminated/exfoliated hybrid, no XRD peak is expected since there is no regular spacing of the platelets. The TEM image shows that the clay layers are individually separated further apart from each other and single platelets are homogeneously dispersed in the polymer matrix.
Principally, the polymer nanocomposites can be synthesized by *in-situ* polymerization [6, 33-35], or polymer intercalation from solution [36, 37]. The effectiveness of the first approach depends on the swelling of the organoclays by the liquid monomers, followed by the polymerization reaction initiated by, for example heat or radiation, a suitable initiator, or a fixed catalyst [38]. The second approach is relied on the adsorption of the polymer chains onto the delaminated clay layers in the solvent. In both methods, the solvent has to be further evaporated and the polymer is trapped within the individual clay platelets resulting in an intercalated and/or exfoliated nanocomposite.

However, for most of the industrially important polymers, these methods are limited because neither a suitable monomer nor a compatible polymer-clay solvent
system is always applicable. The versatile and environmentally benign processing compatible approach based on direct polymer melt intercalation has been introduced by Vaia et al. [39] and became widely used in these days. This approach involves the mixing of organoclay with the polymer at above the softening point of that polymer.

It was suggested that the intercalation would probably be a precursor to exfoliation by shearing action of the screws inducing the delamination of the clay tactoids during processing in the twin screw extruder [40]. In more details, as illustrated in Figure 2-8, the clay tactoids (about 8 micron-sized particle), during the melt mixing, are initially sheared apart into smaller stacks, and the platelets are further peeled apart by the stress transferred from shearing of softened polymer, resulting in the intercalation or, finally, reaching to the exfoliation depending on the affinity of the organoclay and polymer. However, this mechanism cannot be achieved from the optimum processing condition only. More importantly, the organoclay-polymer interaction should be thermodynamically favorable.
In the melt mixing process, in order to avoid the direct incorporation of organoclay (in the form of ultrafine powder) into the polymer during the processing, as well as in order to get an accurate amount of the incorporated fillers, the concentrate or masterbatch two-step approach is a preferred option [31, 41, 42]. First, the masterbatch is formulated by mixing the organoclay with the compatibilizer at the filler loading of about 25 wt.%. At this amount of clay, the masterbatch can be processed and palletized as of the normal resins. This masterbatch (concentrate) is subsequently diluted (i.e., let down) to the desired clay loading by neat polymer resin, Figure 2-9.
2.3 Thermodynamics of Dispersion

In order to delineate the factors controlling the intercalation of polymer/organoclay nanocomposites, thermodynamics’ factors have been discussed by Vaia and Giannelis [43, 44] in terms of both enthalpic and entropic contribution to the free energy. The entropic term refers to the sum of the configuration changes associated with the polymer and the clay, determined using Flory-Huggins lattice-based model. The enthalpic term is expressed by the interaction parameter (by interfacial or surface energies) as energy per area. According to their study, it was summarized that the entropy loss due to the polymer confinement must be compensated by the entropy gained with the interlayer separation by tethered surfactants. If the entropy loss is larger or equal

Figure 2-9: Schematic of polymer/clay nanocomposite preparation via masterbatch two-step melt intercalation process.
to the entropy gain, enthalpy will be the parameter determined whether the intercalation will occur.

The favorable enthalpic change means the interaction between polymer and surface must be higher than the interaction between the surfactant and surface. The associative interactions resulting from these constituents composed of the apolar component [Lifschitz-van der Waals (LW)] and polar component [Lewis acid/base (AB)], described using the following expression [31].

\[
\gamma_{ij} = \gamma_{ij}^{LW} + \gamma_{ij}^{AB} \quad \text{with} \quad \begin{align*}
\gamma_{ij}^{LW} &\approx (\sqrt{\gamma_i^{LW}} - \sqrt{\gamma_j^{LW}})^2 \\
\gamma_{ij}^{AB} &\approx 2(\sqrt{\gamma_i^+} - \sqrt{\gamma_j^+})(\sqrt{\gamma_i^-} - \sqrt{\gamma_j^-})
\end{align*}
\]

The \(i\) and \(j\) subscripts correspond to the various system components (layered silicate \(s\), alkyl surfactant film \(a\), and polymer \(p\)). By using available experimental values, this expression may be useful to identify the appropriate constituents thermodynamically favorable for nanocomposite formation. Based on data from Table 2-3 and the expression above, the dispersion can be achieved when the calculated total surface tension becomes negative (\(\gamma_{ps} > \gamma_{as}\)).
However, for the alkyl surfactant modified clay \((mmt)\) and polyolefins, such as polypropylene (PP) and polyethylene (PE), it is impossible to get the excess enthalpy to promote the dispersion because the surfactant-clay interaction is equal to or significantly more than the polymer-clay interaction.

### Table 2-3: Surface tension components of materials [31].

<table>
<thead>
<tr>
<th>Materials</th>
<th>(\gamma^{LW})</th>
<th>(\gamma^+)</th>
<th>(\gamma^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mmt</td>
<td>66</td>
<td>0.7</td>
<td>36</td>
</tr>
<tr>
<td>Alkane ((C_{12}-C_{18}))</td>
<td>26</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>26</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>33</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

However, for the alkyl surfactant modified clay \((mmt)\) and polyolefins, such as polypropylene (PP) and polyethylene (PE), it is impossible to get the excess enthalpy to promote the dispersion because the surfactant-clay interaction is equal to or significantly more than the polymer-clay interaction.

### 2.4 Synthetic Routes of Polyolefin Nanocomposites

Many attempts have been made in order to improve the dispersion of organoclays in non-polar polymers, such as polyolefins. The most promising way was achieved by introducing the functionalized polyolefin oligomers/polymer modified with maleic anhydride (MA) or hydroxyl group (OH) as a compatibilizer to the organoclay-polymer system [45-49]. It has been believed that these compatibilizers assisted to increase the affinity for the clay and polymer to become more favorable than surfactant/clay interaction. The proposed mechanism, based on the PP-based nanocomposite works, is illustrated in Figure 2-10 that the functionalized PP oligomers (compatibilizer) are first...
intercalated into the organoclay layers. The polar groups of the compatibilizer interact with the oxygen groups of the clay surface via H-bonding. The interlayer spacing of the clay increases and further by the shear stress during the processing the polymer chains can intercalate to the layers. However, the degree of dispersion varies depending on many parameters, for example the ratio of the compatibilizer to the organoclay, the optimum amount of polar functional groups in the molecule, and the processing conditions, from all of which, in order to achieve exfoliation, there should be an optimum between the intercalation capability of compatibilizer in layers, and the miscibility of compatibilizer with the polymer.

Not only maleic anhydride and hydroxyl groups, but other types of compatibilizers, such as sulfonate chloride (SO₂Cl) [50], glycidyl methacrylate (GMA) [51], acrylic acid (AA) [51], di-block copolymers [52], oxidized polyolefin [53] were also used and present in recent publications. It has been found that the structure and dispersion of organoclays in the nanocomposites were mostly a mixture of intercalated and exfoliated structure.
Figure 2-10: Schematic of the dispersion mechanism of the organoclay in the PP matrix with the aid of PP-g-MA [47].
Alternate strategies have been proposed by Manias et al. [54] by introducing functional groups to PP chains mixed with organoclay, and by using neat PP mixed with fluorinated surfactant modified clay. Additionally, Wang et al. [55] improved the dispersion by using ammonium-terminated PP as a modifier to mmt. The nanocomposites formation was achieved from all cases via static melt-intercalation process without mechanical shear. Moreover, the stability of the delamination/exfoliation of these nanocomposites has been investigated.

Moreover, the concern for organoclay dispersion in PE matrix was proposed by Hotta et al. [56] about the effect of number of alkyl chains in the organic surfactant to the dispersion and mechanical properties of nanocomposites. They found that the two-alkyl chain structure was more effective than the single chain by leading to better dispersion of clay in PE matrix and improving their mechanical properties.
3.1 Introduction

The design of antimicrobial materials with a broad spectrum of activity is gaining interest in both academic research and industry to serve in a wide range of applications, for example, medical devices, antifouling coatings, water treatment, textiles, and plastic packaging (food, medical devices, pharmaceuticals, etc.) [57-61]. Despite the required potent effectiveness, antimicrobial materials are desired to be environmentally benign, long-term effective, and cost-reasonable [62].

Among the classes of antimicrobial organic compounds, selected cationic surfactants (composed of a positively-charged head-group and a lipophilic chain structure) have been claimed to be the active compounds in widely-used antimicrobial agents [63]. Based on numerous reports from bacterial studies, such cationic surfactants possess high antimicrobial activity due to a direct insertion mechanism in lipid bilayers, that eventually damages the cell, the bacterial cell wall, the cytoplasmic membrane, or the cytoplasm [63-69]. The general proposed mechanism is that the positively charged ions initially interact with the negative charges on the cell membrane, and subsequently the alkyl chains penetrate into the hydrophobic phospholipid layer, resulting in the loss of selective permeability of the membrane and leading to the leakage of internal constituents, eventually causing cell death [65, 67, 70-73]. In order to fulfill
antimicrobial requirements, several attempts have been made by incorporating these surfactants into polymers and testing against various microorganisms [62, 74, 75].

On a different note, polymer/layered silicate nanocomposites are also currently heavily investigated, because of possible enhancements in thermomechanical performance, barrier properties, an environmentally-friendly flame-retardant character, as well as new functionalities, such as peelable heat-sealing materials.

Recent studies identified antimicrobial activity in organoclays and this new functionality has been recently introduced to polymer/organoclay nanocomposites [76-81]. Most research, along these lines however is not systematic, and it has been focused almost exclusively on the study against bacteria (covering both gram-positive and gram-negative). Here, a more systematic approach is carried out, aiming to identify effective antifungal surfactants, that can also be used as organic-modifications for organo-clays, and ultimately also yield high-performance polymer nanocomposites. We have focused our research efforts on fungi rather than bacteria for various reasons. To date, most of the research regarding antimicrobial properties of materials has focused on bactericidal activity, whereas fungi have received little attention. Fungi are a diverse and complex group of organisms that pose significant problems to society. Fungi comprise important plant, animal and human pathogens, many involved in increasingly relevant human nosocomial infections; toxin producers; common food spoilers and deteriogens, etc., and specifically in food-relevant species of Penicillium spp. and Fusarium spp.

In this chapter, we initially systematically studied the activity of selected free surfactants, and their organoclays (coulombically tethered surfactants) against four species of fungi: Fusarium graminearum, Penicillium citrinum, P.claviforme, and
P. roqueforti, representing important mycotoxinogenic fungal species as well as plant pathogens and common food contaminants.

3.2 Experimental Section

3.2.1 Materials

In order to study the effect of free surfactants on fungal growth, the following commercially available surfactants were chosen: Benzyldimethyldodecyl ammonium chloride (BDDAC), Dimethyldioctadecyl ammonium bromide (DDOAB), Cetyltrimethyl ammonium bromide (CTAB), Poly (5) ethoxylated isodecyloxy propylamine (PEDPA), Octadecyl ammonium bromide (ODAB), and Octadecyl amine (ODA); all are ammonium-based surfactants, which differ in chemical composition and structure (Table 3-1). Their critical micelle concentration and micelle structure are shown in Table 3-2. Sodium bromide (NaBr) was used in the control experiment.

The organically modified clays in this study were Closite® 10A, 15A, and 20A supplied by Southern Clay Products and Nanomer® PGW, I.35L, I.42E, I.28E and I.30E supplied by Nanocor Inc. The Closite® nanoclays based on sodium montmorillonites (Na⁺-mmt, cation exchange capacity = 92 meq/100 g of clay) and Nanomer® nanoclays based on Na⁺-mmt with high CEC (140 meq/100g of clay) are modified by different surfactants at various concentrations. The characteristics of nanoclays are shown in Table 3-3.
Table 3-1: Chemical structures of surfactants.

<table>
<thead>
<tr>
<th>Surfactant name</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzylidimethyldecyl ammonium chloride, BDDAC</td>
<td><img src="image" alt="Chemical structure of BDDAC" /></td>
</tr>
<tr>
<td>Dimethyldioctadecyl ammonium bromide, DDOAB</td>
<td><img src="image" alt="Chemical structure of DDOAB" /></td>
</tr>
<tr>
<td>Cetyltrimethyl ammonium bromide, CTAB</td>
<td><img src="image" alt="Chemical structure of CTAB" /></td>
</tr>
<tr>
<td>Poly (5) ethoxylated isodecyloxy propylamine, PEDPA</td>
<td><img src="image" alt="Chemical structure of PEDPA" /></td>
</tr>
<tr>
<td>Octadecyl ammonium bromide, ODAB</td>
<td><img src="image" alt="Chemical structure of ODAB" /></td>
</tr>
<tr>
<td>Octadecyl amine, ODA</td>
<td><img src="image" alt="Chemical structure of ODA" /></td>
</tr>
</tbody>
</table>
### Table 3-2: Critical micelle concentration (CMC) and micelle structure of surfactants.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Critical micelle concentration (CMC)</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDDAC</td>
<td>$8.80 \text{ mM [82]}$</td>
<td>Sphere</td>
</tr>
<tr>
<td>DDOAB</td>
<td>$0.15 \text{ mM [83]}$</td>
<td>Bilayer</td>
</tr>
<tr>
<td>CTAB</td>
<td>$0.31 \text{ mM [84]}$</td>
<td>Sphere</td>
</tr>
<tr>
<td>ODAB</td>
<td>$0.30 \text{ mM [85]}$</td>
<td>Sphere</td>
</tr>
</tbody>
</table>

### Table 3-3: Nanoclay characteristics.

<table>
<thead>
<tr>
<th>Organic modifier</th>
<th>Modifier concentration (mequiv/100g of clay)</th>
<th>Lab code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Closite® 10A</td>
<td>Dimethyl benzyl hydrogenated tallow quaternary ammonium</td>
<td>125</td>
</tr>
<tr>
<td>Closite® 15A</td>
<td>Dimethyl dehydrogenated tallow quaternary ammonium</td>
<td>125</td>
</tr>
<tr>
<td>Closite® 20A</td>
<td>Dimethyl dehydrogenated tallow quaternary ammonium</td>
<td>95</td>
</tr>
<tr>
<td>Nanomer® I.42E</td>
<td>Dimethyl dehydrogenated tallow quaternary ammonium</td>
<td>140</td>
</tr>
<tr>
<td>Nanomer® I.35L</td>
<td>Poly (5) ethoxylated isodecyloxy propylamine</td>
<td>140</td>
</tr>
<tr>
<td>Nanomer® I.28E</td>
<td>Trimethyl tallow quaternary ammonium</td>
<td>140</td>
</tr>
<tr>
<td>Nanomer® I.30E</td>
<td>Tallow primary ammonium</td>
<td>140</td>
</tr>
<tr>
<td>Nanomer® PGW</td>
<td>None</td>
<td>0</td>
</tr>
</tbody>
</table>
### 3.2.2 Microorganisms

The fungal organisms used for antifungal activity test were *Penicillium cirinum*, *P. claviforme*, *P. roqueforti*, and *Fusarium graminearum*. These fungi were selected from ten tested species. All fungal strains were taken from the Department of Plant Pathology, The Pennsylvania State University.

It is noted that the four fungi used for antimicrobial activity in this study were selected from their fungal growth rate and pigment production. All fungi were inoculated onto the fungal nutrient medium, Potato Dextrose Agar (PDA) and incubated at room temperature. *F. graminearum* and *P. roqueforti* grew faster than *P. claviforme* and *P. citrinum* as shown below.

1. *F. graminearum* (R6574), fastest growth
2. *P. roqueforti*
3. *Aspergillus flavus*
4. *A. Flavus 4-1*
5. *A. Flavus 7-3*
6. *F. oxysporum* (RO122)
7. *F verticillioides* (M3125)
8. *F. oxysporum* (MR6992)
9. *P. claviforme*
10. *P. citrinum*, slowest growth
The characteristics of each selected fungus are presented as follows.

*P. citrinum* has been known as a common fungus of cereal plants like corn, wheat, barley, soybean, and rice [86]. It has been isolated from different environmental conditions, ranging from sediments to agricultural fields and forest soils. Citrinin is a toxic secondary metabolite isolated from *P. citrinum* and acts in animal as a nephrotoxin, damaging the tubules of the kidney [87, 88].

*P. claviforme* has been isolated from barley, air, pepper, and apple juice and puree, as well as soil and dung [89]. The toxins produce by this species are patulin, roquefortine C, 3,12-dihydroroquefortine, oxalin, viridication, cyclopenin, and α-cyclopiazonic acid [90].

*P. roqueforti* has been widely used in fermentation of various types of blue cheeses, but also common as spoilage fungus in refrigerated stored foods, meat and meat products, rye breads, raw milk, and silage [86, 91, 92]. The important toxins are roquefortine C, isofumigaclavine A&B, PR-toxin, and mycophenolic acid [91].

*F. graminearum* has been known as a pathogen of graminaceous plants, in which it causes crown rot and head scab [86]. It is isolated from soil, grasses, seeds of cereals, such as wheat, barley and corn [91]. Numerous toxic compounds, such as deoxynivalenol and its derivatives 3-acetyldeoxynivalenol and 15-acetyldeoxynivalenol, nivalenol and its derivatives, butenolide, culmorin, sambucinol, caloectrin, fusarins, Type A trichotheccenes, including T-2 toxin, HT-2 toxin, diacetoxyscirpenol and neosolaniol have been reported from this species.
3.2.3 Nutrient Media Preparation

All studies consisted of introducing a certain amount of free surfactant (comparable to that contained in a 5 wt.% of organoclay) in a fungal nutrient medium, PDA. The components (free surfactants or organoclays) were added to PDA before autoclaving. The medium solution was sterilized by autoclaving at 121°C for 15 min. The organoclay- or free surfactant-amended nutrient agar was then poured into sterile Petri dishes to provide solidified agar.

In dosage study, at high concentration range, the medium was prepared as described above. For low concentration range, the stock solution of concentrate free surfactant (10 mM) was first prepared and less surfactant concentrations were prepared by diluting the concentrate stock solution with distilled water. The PDA was further added and the volume of solution was adjusted to the desired concentration. The medium solution was sterilized by autoclaving at 121°C for 15 min. The free surfactant-amended nutrient agar was then poured into sterile Petri dishes to provide solidified agar.

3.2.4 Antifungal Evaluation of Surfactants and Organoclays

Four fungal strains, *F.graminearum, P.citrinum, P.claviforme,* and *P.roqueforti,* were inoculated onto the surfactant- or organoclay-amended PDA and the colony growth was determined and compared to the growth on PDA control (without surfactant). Inoculation was done by transferring mycelial plugs from 3-day old colonies growing on PDA medium. All samples were inoculated in a Class II Biosafety cabinet and incubated at room temperature. Antifungal activity was evaluated one day after inoculation and
every day after for one week, by measuring three colony diameters. The average diameter with its standard error was calculated. Antifungal evaluations were reported from three replicates of each sample. All replicates were randomly distributed during the experiment. Each experiment was repeated twice.

3.3 Results and Discussion

3.3.1 Antifungal Activity of Free Surfactants

Figure 3-1 shows the effect of free surfactants on fungal growth. The most effective surfactants were BDDAC and PEDPA. Both BDDAC and PEDPA completely inhibited the growth of all four fungal species while CTAB showed variation depending on the fungal species. However, CTAB still promoted great antifungal activity at 75%, 98%, 100%, and 98% growth reduction of *F.graminearum, P.citrinum, P.claviforme,* and *P.roqueforti,* respectively. From this result, it should be noted that different fungi might display differences in sensitivity even to the same surfactant at identical growing conditions. In this case, *F.graminearum* is the most resistant to CTAB.

The BDDAC surfactant not only possesses the active head group (ammonium) and alkyl chain, but also has an attached benzyl group that could account for enhanced antimicrobial activity [93]. BDDAC is actually a widely-used antimicrobial agent employed, for example, as a pesticide, as a bactericidal in biomedical antiseptic gels, and for sanitization of eating and drinking utensils [94].
DDOAB is a quaternary ammonium compound, like the rest three surfactants used, but it is the only one that possesses two long alkyl chains (Table 3-1). DDOAB had no effect in fungal growth, regardless of the species studied (Figure 3-1). Fungal growth in DDOAB-amended PDA was the same as growth on PDA for most fungi although *P. roqueforti* showed a slight delay in growth in the presence of DDOAB when compared to PDA. This initial slight delay in growth did not reflect in a significant growth difference at 4 days post-inoculation, Figure 3-1 (d). This result contradicts earlier antimicrobial studies on both bacteria and fungi, which showed antimicrobial activity for this same surfactant and suggested alternative mechanisms [95-97]. The alternative mechanism means there is no cell lysis or cell rupture observed for DDOAB (this is a general mechanism for quaternary ammonium salt) but DDOAB causes cell death via a mechanism that does not include cell lysis. It has been proposed that adsorption of DODAB cationic bilayers onto bacterial cells changes the sign of the cell surface potential from negative to positive charge. Positive charge cells do not survive. One possibility explaining the inability of DDOAB to inhibit the growth of these fungal species is that the number of C atoms in each chain might affect the reactivity of the surfactant. It has been reported that the optimum number C atoms (C10-C14) in each chain would promote high reactivity [98]. It is believed that DDOAB molecules do not form a regular micelle like other classical cationic surfactants, however, they assemble as bilayer structures [99]. It seems that DDOAB does not act as a lytic agent because no significant cell leakage has been observed [97]. On the other hand, DDOAB adheres to the cell, it reverses the cell charge from negative to positive, damaging protein function and leading to fungal cell death [97]. However, no cell death was observed from any
fungal species in this study, since fungal growth was not affected when compared with the control PDA.

PEDPA was used in its non-ionic tertiary amine form. The chemical structure of this active surfactant is quite different from the other surfactants with two chains of alcohol-terminated pentaethoxylate, and an undecyl ether. This surfactant showed high effectiveness in growth inhibition of the fungal species targeted in this study. It can stop the growth of all fungal species tested. The motivation for its choice, and the tentative proposed mechanism for its activity, relates to its potential to cause cytoplasmic membrane damage [100].
Figure 3-1: … (continues on next page)
Figure 3-1: Plot of colony diameter versus time of four fungal species in surfactant/PDA samples, (a) *F.graminearum*, (b) *P.citrinum*, (c) *P. claviforme*, and (d) *P.roqueforti*, compared with the PDA control. The BDDAC and PEDPA surfactants show high antifungal activity against all species, followed by CTAB, while DDOAB seems not to inhibit the colony growth of any fungi.
3.3.2 Antifungal Activity of Organoclays

Based on the results obtained in fungal growth studies using free surfactants above, we further studied how these surfactants perform regarding the inhibition of fungal growth in a different situation, i.e. when coulombically-tethered on organoclays.

Figures 3-2 and 3-3 clearly show that surfactants that were efficient in inhibiting fungal growth when in free form (BDDAC and PEDPA), maintained high antifungal activities when attached to montmorillonite (mmt-BDDAC and mmt-PEDPA), although the effectiveness of antifungal activity varied between fungal species. Mmt-BDDAC and mmt-PEDPA displayed a greater ability to reduce growth against *P.claviforme*, and *P.roqueforti* (80-90%), and moderate growth reduction to *P.citrinum*, and *F.graminearum* (40-50% reduction) compared to growth in control PDA. Mmt-CTAB showed high activity only against *P.roqueforti*, Figure 3-2 (d). The BDDAC-modified organoclay was reported to be active against bacterial species tested in a recent report [79].

Although organoclays DDOAB1, 2, and 3 are modified by the same surfactant, they differ in the amount of intercalated and free surfactant within the clays. Namely, mmt-DDOAB1 includes a ~30wt% excess intercalated DDOAB surfactant, while mmt-DDOAB2 is based on the same CEC clay (0.95 meq/g) modified at exchange-capacity (i.e., without any non-tethered intercalated surfactant). Mmt-DDOAB3 is based on a higher CEC mmt (140 meq/100 g) modified also at exchange capacity.

The dialkyl-ammonium modified mmt-DDOAB1-3 showed no mycelial growth reduction for *P.citrinum*, *P.claviforme*, and *F.graminearum*. The higher surfactant
content of mmt-DDOAB1 and mmt-DDOAB3 caused a 31% reduction in the growth of one of the fungal species used: P.roqueforti. The lack of antifungal activity of mmt-DDOAB in this work in consistent with recent studies on gram-negative bacteria [77]. This suggests that organoclays with optimum amount of either free or grafted surfactant can improve an action of mmt-DDOAB, at this point, against P. roqueforti, Figure 3-2 (d). It also means that surfactant transport is not necessary to achieve high antifungal activity, also supported by the rest of the organoclays some of which were repeatedly washed with ethanol and filtered to remove all excess surfactant. Finally, these results emphasized again that the activity of these systems as antimicrobial agents depend upon concentration and the resistance of the fungal species [101].

The quantitative comparison of the antifungal activity between free surfactants and respective organoclays revealed that the surfactants localized on organoclay surfaces exhibited less activity than the free surfactants at the same concentration. It might be possible that the clay-surfactant interaction hinders the interaction between surfactant and the fungal cell. The degree of reduction depended upon the type of organoclays and the evaluated fungal species.

Although colony size changes were not significant with mmt-DDOAB, changes in colony morphology were observed in both F.graminearum, and P.claviforme. The fluffy white colony of F.graminearum, Figure 3-3 (a) was only observed in the PDA control whereas mmt-DDOAB induced the production of highly pigmented mycelium. Spore production decreased for P.claviforme in mmt-DDOAB when compared to that of PDA control and unmodified mmt as shown in Figure 3-3 (c).
Figure 3-2: …(continues on next page)
Figure 3-2: A comparison of antifungal activity between organoclays (mmt-BDDAC, mmt-DDOAB1, mmt-DDOAB2, mmt-DDOAB3, mmt-CTAB, mmt-PEDPA) and their corresponding free surfactants against (a) F.graminearum, (b) P.citrinum, (c) P.claviforme, and (d) P.roqueforti. All surfactants, when they are presented in organoclays, decrease their reactivity compared to free surfactants used at the same concentration.
Figure 3-3: …(continues on next page)
Figure 3-3: Photographs of the colony growth of (a) *F. graminearum*, (b) *P. citrinum*, (c) *P. claviforme*, and (d) *P. roqueforti* in PDA control, unmodified mmt/PDA, and in each organoclay (*mmt*-BDDAC, *mmt*-PEDPA, *mmt*-DDOAB1, *mmt*-DDOAB2, and *mmt*-DDOAB3)/PDA a week after inoculation.
3.3.3 Control Experiments

3.3.3.1 Antifungal Activity of Bromine ion

Any antimicrobial effects due to the presence of halide ions in the surfactant and some halogens, namely, bromide-counterions, must be delineated at this point, since bromine and especially chlorine are widely used for disinfectant purposes [68], it might be plausible that the antifungal activity would be derived from the anion action. In order to test this hypothesis, the fungal cultures were grown in PDA medium containing 5% of sodium bromide ($\text{Na}^+\text{Br}^-$) in the absence of any other free surfactants.

The fungal growth was determined as described above and the results are shown in Figure 3-4. Obviously, the plot of colony diameter against time shows that the growth of all F.graminearum, P.citrinum, P.claviforme, and P.roqueforti inoculated on NaBr/PDA was identical to that of control PDA. It is therefore concluded that the bromide ions have no antifungal activity.
Moreover, we compared the antifungal activity of a primary amine (neutral) and a primary ammonium salt against three of fungal species (P.citrinum was not investigated because of very slow growth). Quaternary ammonium salts and primary ammonium salts, for example cetyltrimethyl ammonium salt and dodecyl ammonium salt have been reported as high reactivity biocides for a long time [64, 102]. Primary amine activity was

3.3.3.2 Antifungal Activity of Octadecayl amine/ammonium

Figure 3-4: A comparison of the antifungal activity between bromide ion in Br⁻/PDA and the PDA control against F.graminearum, P.citrinum, P.claviforme, and P.roqueforti. Bromide ions do not play a role in the antifungal activity.
previously investigated against the bacterium *Staphylococcus aureus* and reports indicated that the reactivity of the amine varied with the hydrocarbon chain length [103]. We wanted to investigate both the effect of these surfactants on the fungal growth and the influence of the charged head group on the antifungal activity. Octadecylamine (ODA) and octadecylammonium bromide (ODAB) were used in this experiment. ODA and ODAB at concentration of 5\%(w/v) were incorporated into PDA media and the fungal species were inoculated and incubated as described above.

Figure 3-5 shows that both the charged and neutral surfactants greatly reduced growth of *Penicillium* species compared to the PDA controls while both acted only moderately against *F. gramineraum*. Moreover, the different head groups of amine and ammonium salts had practically no influence against the fungi tested. It might be thus referred that the head group nature (amine vs. ammonium) is not a critical variation for antifungal efficiency.
3.3.3.3 Antifungal Activity of Unmodified mmt in PDA

Additionally, as a third control, we studied the activity of Na\(^+\)-mmt against the fungi. It was confirmed that most of fungal organisms were not affected by Na\(^+\)-mmt except a small reduction only in colony diameter of *P. roqueforti*, Figure 3-6. Na\(^+\)-mmt, at this concentration of 5%(w/v), has been reported to be significant enough to change the morphology in terms of hyphal structure and colony size of some fungi [104]. We found
no report of this clay destroying the cell of organisms, except the clays possibly influencing nutrient composition and oxygen diffusion. In conclusion, this means Na⁺-mmt without an organic modifier does not play a role as antifungal agent.

Figure 3-6: A comparison between the presence of Na⁺-mmt/PDA and PDA control of the activity against four fungal species, *F.graminearum*, *P.citrinum*, *P.claviforme*, and *P.roqueforti*. Unmodified mmt does not reduce the growth of fungal colonies compared to PDA, except for *P.roqueforti* were an observed growth reduction is observed.
3.3.4 Dosage Study

The objective of this study was to investigate the effect of surfactant concentration and structure on the antimicrobial activity. Dose response measurements for the inhibition of fungal growth was studied over a wide range of concentrations, from below the surfactants’ critical micelle concentration (CMC), to well-above CMC, and including the concentrations corresponding to the surfactant amount found in the organoclay-content of the PDA/organo-mmt experiments. Cationic surfactants, BDDAC, DDOAB, PEDPA, CTAB, and ODAB were amended to fungal nutrient PDA at specific concentrations. The response of three fungal species, *F.graminearum*, *P.claviforme*, and *P.roqueforti*, to each concentration was evaluated by measuring the colonial diameter, and the growth rate ratio was calculated with respect to the control (PDA without surfactant). Three replicates in one experiment were used for each concentration. The result of this inhibition study is shown in Figure 3-7. BDDAC was strongly active in all studied concentrations to all fungal species.
A dose response is clearly seen for PEDPA, CTAB, and ODAB, in which antifungal activity increased with an increased amount of surfactant (as presented in Figure 3-8, 3-9, and 3-10). The effect of concentration in antifungal activity varied with the surfactant structure and the fungal species studied. PEDPA was more effective than CTAB, and ODAB. For PEDPA, the inhibition of fungal growth occurred at concentrations of 0.5-1 mM, while for CTAB and ODAB only concentrations over 40...

Figure 3-7: The fungal growth rate ratio, i.e., the growth rate in the presence of surfactant normalized by the growth rate in PDA, as a function of BDDAC concentration, for *F.graminearum*, *P.claviforme*, and *P.roqueforti*. It is observed that BDDAC shows high effectiveness against all fungi at all concentrations, below its CMC in water to well-above its CMC.
mM inhibited fungal growth. Our interpretation of these results is that antifungal activity systematically increased as the surfactant concentration increased and activity continued to increase even beyond the CMC, when the surfactant molecules are mostly aggregated in micelle structures. Beyond this point, the aqueous solution is a mixture of both free cationic surfactants (at a constant concentration of about CMC) and micelles. However, this result does not agree with a previous report proposing that the highest antimicrobial activity appeared near the CMC, when the highest concentration of free surfactants occurs [105].

Figure 3-8: The ratio of fungal growth rate ratio as a function of PEDPA concentration. This plot shows a pattern of dose response in which the antifungal activity increases with the surfactant concentration until reaching the complete inhibition at about 0.5-1 mM.
Figure 3-9: The fungal growth rate ratio as a function of CTAB concentration. The plot shows a pattern of dose response of moderate activity that the antifungal activity increases with the surfactant concentration.
Figure 3-10: The fungal growth rate ratio as a function of ODAB concentration. The plot shows a pattern of dose response of moderate activity that the antifungal activity increases with the surfactant concentration.
DDOAB is a cationic surfactant forming a bilayer structure, and it did not display antifungal activity against the tested fungal species (previous chapter). In this case, DDOAB could not be completely dissolved in the solution, its antifungal activity as a function of concentration is presented in Figure 3-11. Antifungal activity against *Penicillium* started at very high concentration of DDOAB while *F.graminearum* was not sensitive to this surfactant at any concentration.

Figure 3-11: The fungal growth rate ratio as a function of DDOAB. It is seen that DDOAB is inactive against *F.graminearum* at all tested concentrations. It becomes more active against *Penicillium* at very high concentration (more than 10mM).
3.4 Summary

In this Chapter, the activity of selected free cationic surfactants, and their organoclays (coulombically tethered surfactants) against four species of fungi: *Fusarium graminearum*, *Penicillium citrinum*, *P. claviforme*, and *P. roqueforti* was investigated.

For cationic surfactants with antifungal activity, the important factors that controlled the activity were primarily the chemical characteristics of the surfactants (activity also depended on fungal species tested). All surfactant tested exhibited antifungal properties except DDOAB (which showed antimicrobial activity to *P. roqueforti* at very high concentration only, see Dosage study). BDDAC was the most effective antifungal surfactant against the selected fungi at all concentrations, followed by PEDPA, CTAB, and ODAB (all of which showed definitive dose responses). The charge of head group and the counter anion (i.e. amine, ammonium, and bromide ions) did not seem to play a role in the antifungal activity of this study. Moreover, pristine/unmodified clay (Na⁺-mmt) was not directly responsible for the inhibitory activity. Impressively, the high activity surfactants still maintained their antifungal property even when tethered onto clay particles (limiting surfactant transport).

This study demonstrates a significant novel functionality of organoclays modified with ammonium-based surfactants as antimicrobial agent. This finding may open the way for highly appraised polymer/organoclay nanocomposite technology with the combination of the biocidal property and the enhancement of physical properties.
Chapter 4

Polyethylene/Organoclays Nanocomposites: Antifungal Activity and Mechanical Properties

4.1 Introduction

Despite the very intensive research on polymer nanocomposites, the opportunities of new functionalities made possible by the use of nanofillers still remain largely untapped. Due to an appropriate tailoring prospect of these nanofillers, polymeric properties can be specifically tuned and their desired applications can be achieved.

Polyethylene (PE), a crystalline thermoplastic polymer, is one of the most used polyolefins in a wide range of applications from food packaging films, medical devices, to sealants with peelable or fused seals [106, 107]. The incorporation of nano-fillers, such as organically-modified mmt into PE has been emphasized mostly on an attempt to improve physical properties, including mechanical, thermo-mechanical, and barrier properties.

In this chapter, we present PE/inorganic nanocomposites that exhibit the antifungal activity originating from organo-filler nature (based on the investigation from Chapter3). Specifically, LLDPE/LDPE blend/organically-modified mmt nanocomposites were prepared via melt-processing, and antifungal activity was designed by proper choice of their organic modification. Mmt-based organofillers, which only differ in organic modification, were used to exemplify how these surfactants can be designed to render antifungal activity to the polymer nanocomposites. The comparative discussion of the growth of fungi on unfilled PE and nanocomposite PE films is used to demonstrate how
the antimicrobial efficacy is dictated by the surfactant chemistry and, further, how the nanocomposites’ inhibitory activity compares to that of the organo-fillers and the surfactants.

4.2 Experimental Section

4.2.1 Materials

The organically-modified clays used in this part of the study were Closite® 10A (surfactant content 1.25 mequiv/g), Closite® 20A (surfactant content 0.95 mequiv/g), Nanomer® I44P (surfactant content 1.4 mequiv/g), and Nanomer® I.35L (surfactant content 1.40 meq/g) which are organically modified by BDDAC, DDOAB, DDOAB, and PEDPA, respectively. The matrix was a LLDPE/LDPE blend (PE 808.2, 80/20 blend of linear low density polyethylene/ low density polyethylene, a commercial grade Integral™ polyolefin by Dow). The compatibilizer was polyethylene grafted maleic anhydride LDPE-g-MA (Affinity GA 1900, from Dow Plastics) and was added to enhance the miscibility between the organo-clays and the polymer. The cellophane was also used in this study. The reason is cellophane has porosity so there is no limitation in nutrient availability for colony growth when compared to PE, for example, that will be a barrier limiting nutrient flow from the PDA because it is not porous. That is why the growth on cellophane was the same as in PDA.
4.2.2 Nanocomposite Preparation

A co-rotating twin-screw lab-scale extruder from ThermoHaake was used to compound the clays and the polymers. Organoclays, Closite® 10A, and Nanomer® I.35L were selected to prepare the nanocomposites. A master-batch was first prepared by compounding 60:40 LDPE-g-MA/organoclay with a temperature profile 90, 110, 110, 110, 110°C from feed to nozzle at rotor speed of 40 rpm. In a second extrusion, dilution of the masterbatch by the 80/20 LLDPE/LDPE blend (temperature profile 85, 150, 175 175 °C and 60 rpm) provided nanocomposites with organoclay loadings of 6% and 9 wt.%.

The extrudates were palletized and dried prior to making bar-shaped specimens by injection molding at a temperature of 220 °C. Nanocomposite films were prepared from hot-pressing the injection-molded bars in a Carver Laboratory hot press at a constant temperature of 180 °C and load of 0.5 tons for 10 minute.

4.2.3 Characterization

4.2.3.1 Wide angle X-ray diffraction

Wide-angle X-ray diffraction (WAXD) scans were performed in reflection mode, with an incident wavelength ($\lambda$) of 0.154 nm of CuKα radiation. Measurement was performed for $2\theta$ from 1 to 10 at a scan rate of 1.0°/min. The organoclayes were measured in a powder form, whereas the nanocomposite films were characterized as they were. The layer spacing of the clay was calculated from Bragg’s law, $n\lambda=2d \sin \theta$, where $\lambda$ is
the wavelength of the radiation, \( d \) is the c-dimension distance and \( 2\theta \) is the diffraction angle.

### 4.2.3.2 Transmission Electron Microscope (TEM)

Bright field transmission electron microscope (TEM) images of the samples were obtained with a JEOL 1200 EXII transmission microscope operated at an accelerating voltage of 80 kV, and equipped with a Tietz F224 digital camera. Ultrathin sections (70–100 nm) of the nanocomposites were obtained from cryogenically cutting with an ultramicrotome (Leica Ultracut UCT) equipped with a diamond knife. The sections were transferred to carbon-coated copper grids (200-mesh, with a Lacey support film). No heavy metal staining of sections prior to imaging was done, since the contrast between the fillers and the polymer matrix was sufficient.

### 4.2.4 Antifungal Activity Evaluation

#### 4.2.4.1 Effect of Surfactants and Organoclays on Spore Germination in Broth Culture Solution

The Potato Dextrose Broth (PDB) culture media mixed with free surfactants, or the organoclays were prepared. Organoclays, \( mmt\)-BDDAC (Closite®10A), \( mmt\)-DDOAB1 (Closite®20A), \( mmt\)-DDOAB4 (Nanomer® I.44P), and \( mmt\)-PEDPA (Nanomer® I.35L), were dispersed into PDB solution at the amount of 5%wt/v, while the free surfactants, BDDAC, DDOAB, and PEDPA were added into PDB to get the final
concentration of 10 mM. Both organoclay- and free surfactant- PDB media were further sterilized at 121°C for 15 min and 10 ml was poured into each sterilized test tube. Spore suspension of each fungus was prepared from fungal colonies grown in Potato dextrose agar (PDA). The spores were suspended in sterilized water and adjusted to give a spore concentration of 10⁶ spores/ml. The spores were counted by using a Hemacytometer. Antifungal activity was determined by observing the germination of spores in 10 μl of spore suspension in 10 ml PDB after 1 and 3 days after inoculation by taking a droplet of spores in surfactant- or organoclay-amended PDB, dropping onto a glass slide, and observing the germination under an optical microscope compared to the germination in PDB control. All samples were inoculated at room temperature. Three replicates of each sample were used for antifungal evaluation.

4.2.4.2 Antifungal Activity on Nanocomposite Films

To study the antifungal activity of the cationic surfactants in nanocomposite films, two experiments were carried out. All nanocomposite films and the PE control were cleaned with ethanol and dried at room temperature before testing. All films were placed on the PDA.

In the first experiment, 20 μl of spore suspension in water (spore concentration of 3×10⁵ spores/ml) were gently dropped onto the film surface and the films were then incubated at room temperature. The germination of spores was determined both qualitatively (taking pictures under optical microscope) and quantitatively (counting germinated spores compared to non-germinated spores). Spore germination was
observed under an optical microscope and the percentage of germinated spores was calculated: number of germinated spores was determined relative to non-germinated spores counting from optical micrographs. Three replicates of each sample were used for antifungal evaluation. The experiment was duplicated twice. The spores were counted from 10 optical micrographs taken from three replicates (one experiment). Total of counted spores (germinated and non-germinated spores) was 400 for each sample. The percentage of spore germination was calculated based on this number.

For the second experiment, the spore suspension at the concentration of $3 \times 10^5$ spores/ml was sprayed over the films and PDA control. The incubation was done at room temperature. The germination of spores and growth of hyphae on the nanocomposite films was determined 7 days after inoculation and compared to the controls, which are the unfilled PE films and the sterilized cellophane. It is noted that the cellophane was sterilized by autoclaving in water at 121°C for 15 min before using. Three replicates of each sample were used. The experiment was duplicated twice. Spore counting was not done in this experiment.

### 4.2.5 Mechanical Properties

The mechanical properties of LLDPE/LDPE blend nanocomposites (bulk) were quantified by stress-strain measurements at room temperature using an Instron 5566 testing machine. Tensile testing was performed with 10 kN load cell and mechanical “vise” grips at a cross head speed of 50 mm/min according to ASTM D638. Young’s modulus, tensile strength, and elongation at break have been reported from the
measurement. It was noted that five to ten specimens of each samples were used in order to get statistical data.

4.3 Results and Discussion

4.3.1 Clay Dispersion and Morphology

Figure 4-1 shows X-ray diffractograms of LLDPE/LDPE blend nanocomposites containing 6 wt.% and 9 wt.% of mmt-BDDAC along with a scan of mmt-BDDAC organoclay powder for the comparison. The mmt-BDDAC pattern shows an intense peak at around $2\theta = 4.5$, corresponding to a basal spacing of 1.9 nm, while its nanocomposites show the unexpected result of interlayer gallery decreasing by the observed peak shift to the higher angle. However, similar results have been reported and suggested that the shear stress applied during melt blending process can collapse the interlayer structure of the organoclay [108]. Shah et al. [41] described this as a result of counteracting phenomena of polymer intercalation and alkyl ammonium degradation occurred during the melt processing.

Figure 4-2 shows X-ray diffractograms of LLDPE/LDPE blend nanocomposites containing 6 wt.% and 9 wt.% of mmt-PEDPA along with a scan of mmt-PEDPA organoclay powder for the comparison. The peak at around $2\theta = 3.3$ corresponds to a basal spacing of 2.7 nm, and its nanocomposite peak seems to be disappeared.
Figure 4-1: X-ray diffractograms of *mmt*-BDDAC organocaly and 6 and 9 wt.% of *mmt*-BDDAC/LLDPE/LDPE blend nanocomposites.
Figure 4-2: X-ray diffractograms of mmt-PEDPA organoclay and 6 and 9 wt.% of mmt-PEDPA/LLDPE/LDPE blend nanocomposites.
The TEM is required to confirm the nanocomposite morphologies and the images of selected samples are shown in Figure 4-3. From the low magnification images, it is seen that \textit{mmt}-BDDAC (6 wt.\%) particles are not homogeneously distributed in the LLDPE/LDPE blend. This shows some immiscible character to these systems. The result indicated that \textit{mmt}-BDDAC is immiscible with LLDPE/LDPE blend. The high magnification image shows some intercalation mixed with the fairly large stacks of the clay. This intercalated structure might be due to the interaction of LDPE-g-MA rather than the polymer (LLDPE/LDPE blend) intercalation.
Figure 4-3: TEM images at (a) low and (b) high magnification for 6 wt.% mmt-BDDAC/PE nanocomposite. The scale bars are indicated on the images.
4.3.2 Antimicrobial Activity

According to our previous study of the fungal growth based on hyphal and colony growth, the cationic surfactants BDDAC and PEDPA were claimed to be the most potent antifungal agents against *P.roqueforti*, *P.claviforme*, and *F.graminearum* as both delocalized form, and tethered state on *mmt* surface. The least effective surfactant was found to be DDOAB which did not show antifungal activity against *F.graminearum* but displayed small colony growth reduction of *Penicillium* spp. at very high surfactant concentrations. In the present work, instead of using fungal mycelium, we evaluated the antifungal activity based on the germination and growth of spores in an aqueous suspension, by mixing into broth culture solution and incorporating into the polymer, the activity of these surfactants was studied against the same fungal species and the antimicrobial assay was focused on the germination of spores instead of the growth from hyphal development.

4.3.2.1 Antifungal Activity in PDB

This experiment was an investigation of antifungal activity in broth culture solution, PDB in the presence of surfactants or organoclays. Figure 4-4 presents the antifungal activity of both free surfactants/PDB and organoclays/PDB which were inoculated with the fungal spores. The germination of spores was observed under optical microscope after 1 day and 3 days of inoculation. The result of *P.roqueforti* shown below is identical as *P.claviforme* and *F.graminearum* so results with *P.roqueforti* only are presented hereafter. Both BDDAC and PEDPA promoted strong antifungal activity
when they were used as free surfactant or tethered surfactant in organoclay. The spores remained unchanged and no germination tubes were observed in the spores. DDOAB was still inactive against these fungi and we observed hyphal development from the inoculated spores. From this morphological study, we confirm that the activity of these surfactants against fungal spores was identical to the test against hyphal growth.
Figure 4-4: ...(continues on next page)
Figure 4-4: Optical micrographs (at 400x magnification) of germination from *P. roqueforti* spores in (a) PDB, (b) mmt-DDOAB4 (I.44P), (c) DDOAB, (d) mmt-DDOAB2 (20A), (e) mmt-BDDAC, (f) BDDAC, (g) mmt-PEDPA, and (h) PEDPA surfactant at the beginning of the inoculation, after 1, and 3 days, respectively. Non-germinate spores were observed in the PDB containing BDDAC and PEDPA and their organoclays, while the hyphal growth was found in DDOAB/PDB systems.
4.3.2.2 Antifungal Activity on Nanocomposite Films

Impressively, surfactants that showed high antifungal activity in previous tests (BDDAC and PEDPA) still maintained their inhibitory activity against the tested fungi when tethered on mmt and further embedded in PE nanocomposite films. Figure 4-5 represents the reduction of spore germination on the film surfaces tested against *P.claviforme*. After one week of inoculation, fungal growth was obvious over the PE control and mmt-DDOAB film and mycelium grew beyond the films onto the medium. However, no fungal growth was observed on the mmt-BDDAC nanocomposite films or in the medium surrounding the film, which indicates an inhibition of spore germination or hyphal death soon after spores germinated.

![Figure 4-5](image)

Figure 4-5: A photograph of *P.claviforme* inoculated on PE (control), mmt-DDOAB, 6% mmt-BDDAC, and 9% mmt-BDDAC, respectively. It shows the prevention of spore germination on both 6% and 9% mmt-BDDAC films.

The antifungal activity against *P.roqueforti* was evaluated when the spore suspension was sprayed all over the area of both film and PDA surface. The result is presented in Figure 4-6. As one of the controls, the cellophane was finally entirely
covered by the fungus because of its high porosity and no inhibitory activity. In this result even there was no difference observed between the PE (control), and nanocomposites films, it could not claim that the \textit{mmt}-BDDAC in the films was ineffective. More observations under the microscope are necessary (see the morphological study, Figure 4-8). One might notice that the surfactants were not diffuse from the film. These \textit{mmt}-BDDAC nanocomposite films were effective against the fungal species test in our study.

![Figure 4-6: A Photograph of \textit{P.roqueforti} inoculated on cellophane, PE (control), 9\% \textit{mmt}-BDDAC, and \textit{mmt}-DDOAB respectively.](image)

Differences in spore germination on PE nanocomposites that included different amounts of organoclay, \textit{mmt}-BDDAC and \textit{mmt}-PEDPA, (6\% and 9\%,w/w), 6\% \textit{mmt}-DDOAB, and a PE control are presented in Figures 4-7, 4-8, and 4-9 for \textit{P.claviforme}, \textit{P.roqueforti}, and \textit{F.graminearum}, respectively. \textit{mmt}-BDDAC films inhibited spore germination of \textit{Penicillium} spp. on the film surface. No hyphae developed on films while extensive mycelial growth was observed on both the PE control and on 6\% \textit{mmt}-DDOAB nanocomposite films.
PE nanocomposite with mmt-PEDPA also showed great activity against *P. claviforme* and *P. roqueforti*. These results indicated that the antifungal activity of this nanocomposite depends on the incorporated concentration of the surfactant in organoclay. High concentration of mmt-PEDPA (9% wt) markedly promoted the antifungal activity. As shown in Figure 4-7 and 4-8, after several days after inoculation with the spore suspension, some hyphae started to develop on 6%mmt-PEDPA films, however, this was a small proportion compared to the amount of inoculum applied.
Figure 4-7: ...(continues on next page)
Figure 4-7: Optical micrographs of the germination of *P. claviforme* spores on PE control, 6%*mmt*-DDOAB, 6%*mmt*-BDDAC, 9%*mmt*-BDDAC, 6%*mmt*-PEDPA, and 9%*mmt*-PEDPA nanocomposite films. These illustrate the growth after 2, 3, and 5 days of inoculation 20 μl of 3×10^5 spores/ml at 100x magnification. *mmt*-BDDAC (6% and 9%) and 9%*mmt*-PEDPA completely inhibited spore germination.
Figure 4-8: …(continues on next page)
On the other hand, it seems that both mmt-BDDAC and mmt-PEDPA films did not exhibit antifungal activity against *F. graminearum* even though these surfactants showed moderate efficiency in their organoclay form. Figure 4-9 shows spore germination 36 hours after inoculation, spore germination was observed on all types of films and increased with the time.
Figure 4-9: ...(continues on next page)
Figure 4-9: Optical micrographs of the germination of *F. graminearum* spores on PE control, 6%*mnt*-DDOAB, 6%*mnt*-BDDAC, 9%*mnt*-BDDAC, 6%*mnt*-PEDPA, and 9%*mnt*-PEDPA nanocomposite films. This illustrates the growth after 10, 20, and 36 hours of inoculation 20 μl of 3×10^5 spore/ml at 200X magnification. Both *mnt*-BDDAC and *mnt*-PEDPA nanocomposite films do not exhibit ability to inhibit spore germination in *F. graminearum*, although there was a delay in germination, hyphal growth and germination percentage.
It might be implied that the activity of surfactant may vary with the fungal species and their spore characteristics, e.g. cell wall structure, robustness, germination time, although this hypothesis needs to be tested further. The surfactant concentration was another parameter controlling the antifungal activity, and based on the experiments above appropriate amount could promote strong inhibitory efficiency, even when surfactants were tethered on clay layers [78, 109]. Two mechanisms have been proposed as responsible for the antimicrobial activity: leaching of antimicrobial agents (surfactant) and from the surfactant tethered on the clay surface [110, 111]. The latter mechanism was proved to be mainly responsible for antimicrobial activity by Herrera, et al. that alkyl chain interacted to phospholipid layer and positive charge attracted to negative bacterial cell wall via electrostatic interactions [110]. As a filler in nanocomposite films, the dispersion as well as the migration of organoclays to the film surface are probably important parameters that should be considered in achieving consistent antifungal activity on the film surface.

Finally, the antifungal activity was quantitatively evaluated by counting the number of germinated/non-germinated spores and calculating the percentage of spore germination. For *F.graminearum*, the germ tubes can be observed after 10 hours and at 48 hours for *Penicillium* spp. The result in Table 4-1 indicates that for *F.graminearum*, at early stages of germination (10 hours), a difference in spore germination was observed. The percent germination on the nanocomposite films was consistently lower than that on the PE control. These surfactants might affect the cells at early steps of germination but they do not kill the cell and stop the growth.
4.3.3 Mechanical Properties

Table 4-1 shows the tensile properties of LLDPE/LDPE/organo-mmt nanocomposites and LLDPE/LDPE pure (unfilled) blend. All nanocomposites exhibit higher tensile modulus than that of the unfilled blend. The value of tensile modulus increased by 8, and 4% using 6 and 9 wt% of mmt-BDDAC, respectively, and 16 and 5% using 6 and 9 wt% of mmt-PEDPA, respectively. However, the tensile strength of the PE nanocomposites is lower when the organoclays were added compared to the unfilled PE. It is noticed that these organoclays (mmt-BDDAC and mmt-PEDPA) might not be suitable choices for mechanical property enhancement, specifically, when compared to the tensile value from previous work that mmt-DDOAB substantially improved the mechanical properties of PE blend by increasing the tensile Young’s modulus up to 139% and did not change the tensile strength of the samples [112].

Table 4-1: Percentage of spore germination on the PE and PE nanocomposite films.

<table>
<thead>
<tr>
<th>Fungi</th>
<th>Timeᵃ</th>
<th>Spore Germination (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PE</td>
</tr>
<tr>
<td>F.graminearum</td>
<td>10</td>
<td>46</td>
</tr>
<tr>
<td>P.claviforme</td>
<td>48</td>
<td>5</td>
</tr>
<tr>
<td>P.roqueforti</td>
<td>48</td>
<td>7</td>
</tr>
</tbody>
</table>

ᵃ hours after inoculation
Table 4-2: Tensile properties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Yield strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE (no filler)</td>
<td>273 ± 6</td>
<td>26 ± 1</td>
<td>10 ± 1</td>
<td>342 ± 17</td>
</tr>
<tr>
<td>PE+6%mmt-BDDAC</td>
<td>294 ± 22</td>
<td>18 ± 0.2</td>
<td>13 ± 0.1</td>
<td>251 ± 7</td>
</tr>
<tr>
<td>PE+9%mmt-BDDAC</td>
<td>284 ± 4</td>
<td>16 ± 0.2</td>
<td>12 ± 0.1</td>
<td>267 ± 16</td>
</tr>
<tr>
<td>PE+6%PEDPA</td>
<td>318 ± 9</td>
<td>16 ± 0.2</td>
<td>12 ± 0.1</td>
<td>188 ± 3</td>
</tr>
<tr>
<td>PE+9%PEDPA</td>
<td>286 ± 13</td>
<td>14 ± 0.2</td>
<td>11 ± 0.2</td>
<td>209 ± 6</td>
</tr>
</tbody>
</table>
4.4 Summary

In this Chapter, LLDPE/LDPE/organoclay nanocomposites were prepared by melt compounding of masterbatches (based on LDPE-g-MA and organo-\textit{mmts}, which were \textit{mmt}-BDDAC, and \textit{mmt}-PEDPA, respectively), and their antifungal activity, as well as mechanical property were investigated compared to unfilled PE blend and \textit{mmt}-DDOAB/PE nanocomposites. The organo-\textit{mmts} were selected based on their great antifungal performance presented in the previous chapter.

Here, more impressively, even as the fillers in the nanocomposite films, surfactants still maintained the activity against the \textit{Penicillium} spp. It seems the amount of organoclay is one of the important parameters to control the activity. However, the activity against different fungal species was differently promoted. For the non sensitive fungus, \textit{F.graminearum}, these potent surfactants presented small activity only at the early stages of germination based on the quantitative study.

Mechanical properties, including tensile Young’s modulus, tensile strength and elongation at break were investigated. It was found that these organoclays (\textit{mmt}-BDDAC and \textit{mmt}-PEDPA) were not the appropriate choices for mechanical property enhancement of this PE blend.

It is summarized that the PE/organoclay (\textit{mmt}-BDDAC and \textit{mmt}-PEDPA) nanocomposites have the potential for being used as antimicrobial materials. However, the organoclay dispersion and mechanical properties of these nanocomposites need to be improved.
Chapter 5

Optimization of HDPE Organoclay Nanocomposites’ Mechanical Performance

5.1 Introduction

Reinforcement optimization of polymer/mmt nanocomposites can be achieved by fine dispersion (exfoliation) and high clay/polymer interfacial affinity [52]. Dispersion of mmt in polyolefin matrices can be achieved by adding polar functional group to the polymers, such as maleic anhydride (MA), and equivalently functionalized polymers used as a ‘compatibilizer’ (for example, in the form of MA-polymer/organo-mmt masterbatch) [45-47, 113]. Thus, even upon dilution of the masterbatch by a non-functionalized matrix the functional-polymer compatibilizer, such as PE-grafted-maleic anhydride, can becomes a measurable component in the polyolefin/clay nanocomposites, especially if high mmt loading is desired. There have been many reports which show that the maleic anhydride content and the ratio of organoclay to PE-g-MA are important parameters promoting filler interactions and miscibility with the polymer matrix [45, 114-117], and consequently property improvements in the nanocomposites.

In the case of polyolefins, the influence of molecular weight and crystallinity of these compatibilizers (especially with respect to the polymer matrix characteristics) and their effect on the mechanical properties improvements has not yet been definitively shown. In previous work in this laboratory, HDPE/HDPE-g-MA/organoclay nanocomposites have been prepared by masterbatches (HDPE-g-MA/1.44P organoclay)
employing two different HDPE-g-MAs (Polybond-3009, termed Y, and Arkema Orevac 18307, termed X) combined with three different HDPE matrices of varied Mw and density (crystallinity). Subsequently, the mechanical properties of the HDPE nanocomposites (at 0.2, 0.5, 1, 3, and 6% clay content) have been investigated. It was found that low Mw HDPE-g-MA (low viscosity, high melt index) promoted better mechanical reinforcement compared to higher viscosity HDPE-g-MA, indicating kinetic and co-crystallization mechanisms to be dominant.

Here, this project was completed by testing a third masterbatch system, based on Amplify GR 205 (HDPE-g-MA with intermediate characteristics compared to the previously two tested HDPE-g-MAs, termed Z) compounded with the same three HDPE matrices. We also prepared the nanocomposites by using a single-step process of injection molding mixed pallets of matrix and master-batch, instead of a two-step process (employing first extrusion for the let-down of the masterbatch, and subsequently injection molding) and compared the mechanical properties of these nanocomposites, cf. effects of processing conditions.

The aim of this part of the work, is to correlate the crystallinity and Mw characteristics of the HDPE-g-MA (especially with respect to the characteristics of the HDPE matrix) and develop design-principles for appropriate HDPE-g-MA and HDPE pairing that will achieve optimum polymer nanocomposite mechanical performance (largest mechanical reinforcement, no loss of crystallinity, etc.) in connection with the associated changes in crystallization and mechanical properties.
5.2 Experimental Section

5.2.1 Materials

Commercial grade polymers and fillers were used throughout this study. Three commercial high density polyethylenes (HDPE) were used, MarFlex 9659, Marflex TR-130, and an experimental Nova grade with high density and high-barrier. The commercial compatibilizers, HDPE grafted maleic anhydride (HDPE-g-MA), used were Arkemar Orevac 18307, Chemtura/Crompton Polybond 3009, and Dow Amplify GR205. The characteristics of all polymers and compatibilizers are presented in Table 5-1. The organoclay used was Nanomer® 1.44P; a medium CEC (ca.1 meq/gr) montmorillonite modified with dimethyl ditallow ammonium (exchanged at capacity, ca.35 wt% surfactant in the organo-mmt).

Table 5-1: Characteristics of HDPE and HDPE-g-MA.

<table>
<thead>
<tr>
<th>HDPE</th>
<th>Lab code</th>
<th>Melt index (MI)</th>
<th>MA (wt%)</th>
<th>$M_w$ (g/mol)</th>
<th>$\rho$ (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial name</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MarFlex 9659</td>
<td>A</td>
<td>1</td>
<td>0</td>
<td>84000</td>
<td>14700</td>
</tr>
<tr>
<td>MarFlex TR-130</td>
<td>C</td>
<td>0.3</td>
<td>0</td>
<td>123000</td>
<td>16600</td>
</tr>
<tr>
<td>Nova</td>
<td>D</td>
<td>$\approx$1</td>
<td>0</td>
<td>$\approx$84000</td>
<td>14500</td>
</tr>
<tr>
<td>Arkema Orevac 18307</td>
<td>X</td>
<td>2.5 (230°)</td>
<td>&lt;1</td>
<td>74000</td>
<td>9000</td>
</tr>
<tr>
<td>Chemtura/Crompton Polybond 3009</td>
<td>Y</td>
<td>5</td>
<td>1</td>
<td>71000</td>
<td></td>
</tr>
<tr>
<td>Dow Amplify GR 205</td>
<td>Z</td>
<td>2</td>
<td>1.2</td>
<td>76000</td>
<td></td>
</tr>
</tbody>
</table>
\[ 1/MI = -4.04114 + 0.00006M_w \quad [118] \]

\[ \eta = KM_w^\alpha \quad \text{where} \quad K = 62\text{ml/g}; \quad \alpha = 0.70 \quad [119] \]

In conjunction with the single-letter identification for the various polymers, a series of systematic acronyms were used to represent the masterbatches and the HDPE nanocomposites. The construction of the acronyms is as following, with the letters and numbers specifying the types of HDPE, HDPE-g-MA, organoclay, and the amount of the organoclay in the masterbatch and the clay in the nanocomposites, respectively:
5.2.2 Nanocomposite Preparation

All series of HDPE/clay nanocomposites were prepared via the dilution of concentrates (masterbatches) by neat HDPE, a two-step process. First, the masterbatch was prepared by dispersing 40 wt.% organoclay I.44P in 60 wt.% HDPE-g-MA; corresponding to ca. 24 wt. % montmorillonite and 16 wt. % organic modifier loading in the masterbatch (this was the maximum inorganic loading that we could process in our equipment and still obtain a “resin”-looking masterbatch). This masterbatch was further diluted by extrusion in neat HDPE in order to obtain the nanocomposites. The melt processing of the masterbatch and its dilution were carried out in a co-rotating twin-screw lab-scale extruder from ThermoHaake at a temperature profile of 175°, 175°, 175°, and 175°C from feed to nozzle, at a rotor speed of 50 rpm, providing nanocomposites with clay loadings of 0.2, 0.5, 1, 3 and 6 wt.% inorganic. In order to prepare the dogbone- and bar-shaped specimens for tensile and flexural test, the palletized nanocomposite extrudates were molded by Injection molding at the temperature profile of 230°, 230°, and 230 °C from feed to nozzle (Boy 25ton lab-scale injection molder). It is noted that all resins and extrudates were dried under vacuum at 70°C for 14 hours before melt processing steps.

A single step process (Injection molding only) was also used to prepare selected nanocomposites, AYI40, and all HDPEs/ZI40 systems by melt-mixing of polymer pellets and the masterbatch without the extrusion let-down processing. The mechanical characterization was compared with the two-step process nanocomposites.
5.2.3 Characterization

5.2.3.1 X-ray diffraction

Wide-angle X-ray diffraction (WAXD) scans were performed in reflection mode, with an incident wavelength ($\lambda$) of 0.154 nm of CuKα radiation. The measurement was performed for $2\theta$ from 1 to 10 at a scan rate of 1.0°/min. The organoclay was directly measured from its powder, whereas the masterbatches and nanocomposites were characterized from the injected specimen surface. The 001 layer spacing of layered silicate were calculated from Bragg’s law, $n\lambda=2d \sin \theta$, where $\lambda$ is the wavelength of the radiation, $d$ is the interplanar (hkl) distance and $2\theta$ is the diffraction angle of the first peak.

5.2.3.2 Differential Scanning Calorimetry (DSC)

The melting temperature, the crystallization temperature, and the crystallinity of neat HDPEs, HDPE-g-MA and HDPE nanocomposites were evaluated using differential scanning calorimetry (DSC), by a TA instrument DSC Q100, operated in nitrogen. The samples were cyclically heated and cooled between 40-180°C at a rate of 10°C/min. The area of the endotherm peak was determined and the heat of fusion was calculated by comparing the area of the sample and that of the standard. The degree of crystallinity was then calculated by comparison with the heat of fusion of a perfectly crystallized polyethylene, i.e., 298 J/g [120].
5.2.4 Mechanical Testing

The mechanical properties of the nanocomposites were quantified by both tensile and flexural stress-strain measurements at room temperature using an Instron 5566 testing machine. Tensile testing was performed using dogbone-shaped specimen with 10 kN load cell and mechanical “vise” grips at a cross head speed of 50 mm/min according to ASTM D638. The Young’s modulus, tensile strength, and elongation at break have been reported from the tensile test. The flexural test was performed by using bar-shaped specimen with three point bend method at a testing rate of 5 mm/min according to ASTM D790. Flexural modulus, flexural yield strength, and strain at yield have been reported from the test. It was noted that five to ten specimens of each sample were used in order to calculate values with acceptable statistical errors.

5.3 Results and Discussion

5.3.1 Structural Characterization

XRD scans of the organoclay, I.44P, and their X and Y based masterbatches (both at 40 wt% organo-mmt, named XI40 and YI40) are presented in Figures 5-1, and 5-2, respectively. The XI40 system showed a definite shift to lower angle in the intensity of the diffraction peak, corresponding to the (001) plane reflection of the clay, indicating an increase of the interlayer spacing of the clay from the X intercalation, while there was no peak shift for YI40 masterbatch indicating interlayer spacing of clay remained at the same position as before dispersion (intercalation/exfoliation). It seems, from the
calculation reported in Table 5-2, the organoclay I.44P was better dispersed in X-HDPE-g-MA than that in Y-HDPE-g-MA, as the c-dimension seems to have increased. The same trend seems to persist for the respective nanocomposites, albeit to a substantially smaller extent; namely, at high filler loadings the X-based nanocomposites seem better dispersed than the Y-based ones, whereas at low filler loadings the XRD-measured dispersion is the same between X and Y masterbatches.

Figure 5-1: X-ray diffractograms of I.44P organoclay and its X masterbatch (XI40). The peak shift to the lower angle means that the intercalation of X increases the spacing between the clay galleries. This organoclay I.44P was well dispersed in X-HDPE-g-MA and highly-disordered (low 001 intensity, broad diffraction peak, high low-2θ background intensity).
Figure 5-2: X-ray diffractograms of I.44P organoclay and its Y masterbatch (Y140). The dispersion seems worse than before, a definitively intercalated 001 peak, but the disorder is markedly smaller than in X- masterbatch (higher-intensity and narrower 001 peak).
The X-ray diffractograms of the HDPE nanocomposites are illustrated in Figures 5-3 to 5-5 for all HDPEs (A, C, and D) with X based nanocomposites which show intercalated peaks at all clay concentrations. The morphology of HDPE nanocomposites was probably the combination of intercalated structure and aggregated tactoids (confirmed by direct TEM observation in another study). The exfoliated clay platelets dominate the low concentration clay composites, e.g. at 0.2 and 0.5 wt. % mmt.

Table 5-2: XRD data of the 001 diffraction of the organoclay and the two masterbatches.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$2\theta_{001}$ (degree)</th>
<th>d-spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.44P organoclay</td>
<td>3.50</td>
<td>2.50</td>
</tr>
<tr>
<td>XI40</td>
<td>&lt; 1.6</td>
<td>&gt; 5.5</td>
</tr>
<tr>
<td>YI40</td>
<td>3.5</td>
<td>2.50</td>
</tr>
</tbody>
</table>
Figure 5-3: X-ray diffractograms of XI40 masterbatch and its HDPE-A nanocomposites. The intercalated peaks are found at all clay concentrations. The exfoliated structure probably dominates at low clay contents.
Figure 5-4: X-ray diffractograms of XI40 masterbatch and its HDPE-C nanocomposites. The intercalated peaks are found at all clay concentrations. The exfoliated structure may present at low clay contents.
Figure 5-5: X-ray diffractograms of XI40 masterbatch and its HDPE-D nanocomposites. The intercalated peaks are found at all clay concentrations. The exfoliated structure may present at low clay contents.
Figures 5-6, 5-7, and 5-8 present X-ray diffractograms of Y based masterbatch and its nanocomposites of HDPE-A, -C, and –D, respectively. The dispersion of clays in the HDPE-A nanocomposites (Figure 5-6) seems similar as before, a mixed intercalation/exfoliation. Moreover, the stronger intercalated peaks may suggest slightly worse dispersion of this system compared to HDPE-A in X based nanocomposites. As shown in Figure 5-7, and Figure 5-8, both HDPE-C and HDPE-D nanocomposites present better dispersion, probably, as good as in their X based masterbatch system.

Figure 5-6: X-ray diffractograms of Y140 masterbatch and its HDPE-A nanocomposites. The dispersion seems similar as before (intercalated/exfoliated), and maybe slightly worse than that in the X140 based masterbatch (stronger intercalated peak).
Figure 5-7: X-ray diffractograms of Y140 masterbatch and its HDPE-C nanocomposites. The dispersion seems similar as before (intercalated/exfoliated), and probably as good as that in the X140 based masterbatch.
Figure 5-8: X-ray diffractograms of YI40 masterbatch and its HDPE-D nanocomposites. The dispersion seems similar as before (intercalated/exfoliated), and probably as good as that in the XI40 based masterbatch.
5.3.2 Thermal Characterization

The thermal properties, in particular melting and crystallization, of the HDPE nanocomposites were characterized by differential scanning calorimetry (DSC) and were compared to the unfilled equivalents. The nanocomposites of different HDPE grades (A, C, and D) combined with XI40, YI40, and ZI40 based masterbatches exhibited the common behavior for polyolefins reinforced by organically modified mmt: Specifically, the melting temperature ($T_m$), shown in Table 5-3, of all nanocomposites was largely unaffected by the clay at all concentrations compared to the unfilled equivalents. From this result, it may be implied that the organoclay and HDPE-g-MA do not alter the crystal structure, i.e., the crystal unit cell, of HDPEs upon the nanocomposite formation. This is a typical trend of polyolefin –PE and PP– reinforced by alkyl-ammonium organoclays.

The nucleation can be inferred, in a first approximation, from the crystallization temperature ($T_c$) given the unaltered $T_m$, DSC scans showed also an unchanged $T_c$ for all nanocomposite systems, indicating that the organoclay shows no appreciable heterogeneous nucleation effect, which is a rather uncommon behavior for organoclay/polyethylene nanocomposites [121, 122]. However, this behavior is coincided with the observation from some previous publications [123, 124]. There have been reports proposed that the nucleating ability of clay on the crystallization of PE is much dependent on the degree of dispersion of the clay filler: intercalated clay function as a retardant, while exfoliated clay is a nucleant [125, 126]. Also, in the present study the use of HDPE-g-MA, which is expected to be in the immediate vicinity of and wet the mmt, can also hinder the ability of the inorganic particles to heterogeneously nucleate
HDPE crystals. According to the unchanged $T_c$ value, neither marked nucleating nor substantial retarding effects from the clay filler was observed in the crystallization of our nanocomposites, based on scanning DSC experiments. More appropriate, isothermal crystallization studies are needed to elucidate the clays’ effect on crystallization, however such an investigation goes beyond the scope of this work.
Table 5-3: Differential Scanning Calorimetry (DSC) data for neat HDPE and HDPE nanocomposites (subscripts 1 and 2 indicate first and second heating cycle).

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It must be emphasized that the above DSC study is not intended to elucidate the crystallization behavior of the nanocomposites per se, it is only intended to provide the crystal fractions ($\Phi$) and $T_m$, $T_c$, so as to interpret any changes in the mechanical properties (vide infra). Along these lines, all above crystal fractions are based on $\Delta H$ reported per mass of polymer (rather than the usual per mass of sample).

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5.3.3 Mechanical Properties

5.3.3.1 Two-step process

Tensile properties, including tensile/Young’s modulus, tensile strength, and elongation at break, as well as flexural properties, including flexural modulus, flexural stress at yield, and flexural strain at yield of HDPE-A, -C, and -D nanocomposites combined with XI40, YI40, and ZI40 based masterbatches, are compared to that of unfilled equivalents in Figures 5-9, 5-10, 5-11, 5-12, 5-13, and 5-14.

The incorporation of the organoclay to the HDPE matrices resulted in substantial increases of the tensile modulus of the nanocomposites with respect to unfilled HDPEs, as expected. The modulus of all nanocomposite systems was consistently increased with increasing amount of clay added into the polymer matrices. This enhancement can be explained, in the simplest approach based on the fundamentals of conventional composites, along the lines of the clay fillers acting as reinforcing elements, and leading to an increase in the rigidity of the HDPE in the nanocomposites. Moreover, in case of intercalated/exfoliated features in polymer nanocomposites, the high surface area of the clays in combination with the strong interactions of the MA groups in the X,Y, and Z functional polymers, are expected to result in additional enhancement of the tensile modulus through the formation of polymer-stabilized filler-networks [127, 128].

From our study, the modulus was improved in all HDPE nanocomposites, however, the degree of improvement varied depending on the type of HDPE and also on the masterbatch HDPE-g-MA pairing (cf. Mw and density). As expected, based on the comparison of the different HDPEs in the same masterbatch, the high molecular weight
HDPE-C nanocomposites in each masterbatch showed the highest improvement in tensile Young’s modulus (at the highest attained value of 104% for sample C60ZI40), while the lower molecular weight polymers, HDPE-A and -D showed less increase of these values (at the maximum value of 44% and 31% for samples A60YI40, and D60YI40, respectively). However, the tensile modulus of both HDPE-A, and –D nanocomposites have been approaching the theoretical maximum of 2 GPa, a limit that corresponds to the HDPE-g-MA energy of adsorption on mmt. It has been suggested before that high molecular weight polymer matrix can promote better dispersion of organoclay [42, 108, 129, 130]. As the viscosity of the molten polymer matrix phase increased, the shear stress imposed by the polymer is increased, which in turn facilitated the dispersion of organoclay agglomerates. Accordingly, the finer dispersion led to better modulus improvement.

The value of the tensile strength of the nanocomposites did not exhibit significant variation compared to the equivalent unfilled HDPEs. Only small increases of the tensile strength were observed with higher clay content. The elongation-at-break showed a deviation (increasing or decreasing) depending on the system details. Namely, it is seen that the choice of masterbatch systems, which differed in the characteristics of the HDPE-g-MA used, played an important role: Apparently, from the comparison between each polymer-masterbatch system, a $M_w$ and density matching between the selected HDPE matrix and the MA-functionalized-HDPE in the masterbatch showed the greatest enhancement of the “tensile” properties (simultaneously improving the modulus and maintaining the ductility of the polymers).
According to the comparison of the same HDPE with different masterbatches, it was observed that the YI40 masterbatch may be an appropriate choice for improving mechanical properties of HDPE-A, (Figure 5-9), due to the greatest increase of tensile modulus (44% at 6% wt. clay loading), and smallest decrease of elongation at break (about 7%) at 0.2, 0.5, and 1% wt. of clay content. Additionally, superior improvement of elongation was found at 3% and 6% wt. clay content of sample A30YI40 and A60YI40, that the values slightly increased to about 7%, and 15%, respectively, compared to the unfilled HDPE-A, while AXI40 and AZI40 nanocomposites did not show the improvement of elongation at break (Appendix A).

Similar trends were observed for HDPE-C nanocomposites (Figure 5-10) that the YI40 based masterbatch was an appropriate choice to enhance their tensile performance. Although, the XI40 and ZI40 masterbatch improved more the modulus of HDPE-C than that of the YI40 based system (83%, 105%, and 60% for C60XI40, C60ZI40, and C60YI40, respectively), Figure 5-10, this reinforcement was at the expense of a compromised elongation at break at all clay contents of CYI40 nanocomposites.

Additionally, the YI40 masterbatch markedly improved the tensile modulus of HDPE-D nanocomposites (Figure 5-11), as well as the ZI40 masterbatch, by increasing the modulus up to about 30% (D60YI40, and D60ZI40) compared to the unfilled HDPE-D. However, it was observed that the YI40 based masterbatch showed better improvement in the elongation at break than that of the XI40 and ZI40 based masterbatches, specifically, the maximum elongation at break 243% for D30YI40 compared to 2% and 103% for D30XI40, and D10ZI40, respectively.
According to this result, and in light of the mostly unaltered behavior shown in the crystallinity of the composites, it can be surmised that an appropriately selected MA-functionalized HDPE is the most important factor to control the performance of the polymer nanocomposites. The general observation from this study is that the Y140 masterbatch enhances the mechanical properties of all HDPEs with balancing between modulus improvement and ductility sacrifice. In other words, the lower molecular weight HDPE-g-MA better improves the mechanical properties than the higher molecular weight functional polymers.
Figure 5-9: Plot of relative Young’s modulus, relative tensile strength, and relative elongation at break versus the clay content for AXI40, AYI40, and AZI40 compared to the unfilled “A”. The AYI40 nanocomposites show the best mechanical enhancement by the greatest improvement in modulus and the least sacrifice in elongation at break.
Figure 5-10: Plot of relative Young’s modulus, relative tensile strength, and relative elongation at break versus the clay content for CXI40, CYI40, and CZI40 nanocomposites compared to the unfilled “C”. The CYI40 nanocomposites show the best mechanical enhancement. Even though they do not promote the highest modulus, they do show the least sacrifice in elongation at break.
Figure 5-11: Plot of relative Young’s modulus, relative tensile strength, and relative elongation at break versus the clay content for DXI40, CYI40, and DZI40 nanocomposites compared to the unfilled “D”. DYI40 and DZI40 nanocomposites show the greatest improvement in modulus, while the DYI40 shows slightly better elongation at break than DZI40.
Focusing on the flexural behavior: the comparison of HDPE-A, -C, and -D nanocomposites, the flexural modulus increased with higher amount of nanofillers, paralleling the tensile behavior. Also similar to the tensile/Young’s modulus trends, HDPE-C nanocomposites showed the highest improvement of flexural modulus at about 95% for the C60XI40 composite, compared to the unfilled “C”. The CYI40 and C2I40 also presented high improvement, of 92% and 88% respectively. The flexural modulus improvement of HDPE-A, and –D nanocomposites presented the highest flexural modulus improvement, at 75% and 28%, for A60ZI40 and D60YI40, respectively. As expected, the flexural yield stress and the flexural strain at yield were not significantly affected by the filler amount. A slight increase in yield stress was found for the highest clay contents used.

However, from the flexural deformation studies, neither the choice of maleic functionalized HDPE masterbatches (XI40, YI40, and ZI40), nor their ‘matching’ to their HDPE matrices, was clearly manifested in the nanocomposites’ flexural stiffness. This lack of measureable differences probably reflects that the flexural modulus directly depends on the amount of filler, rather than other variables, for example Mw, and/or density of the polymers. This is not a surprising result since, compared to the tensile measurements, flexural studies are much slower and are sensitive to the deformation of much larger length-scales.
Figure 5-12: Plot of relative flexural modulus, relative flexural yield stress, and relative flexural yield strain versus the clay content for AXI40, AYI40, and AZI40 nanocomposites compared to the unfilled “A”. The flexural properties seem not to be influenced by the types of masterbatches.
Figure 5-13: Plot of relative flexural modulus, relative flexural yield stress, and relative flexural yield strain versus the clay content CXI40, CYI40, and CZI40 nanocomposites compared to the unfilled “C”. The flexural properties seem not to be influenced by the types of masterbatches.
Figure 5-14: Plot of relative flexural modulus, relative flexural yield stress, and relative flexural yield strain versus the clay content for DXI40, DYI40, and DZI40 nanocomposites compared to the unfilled “D”. The flexural properties seem not to be influenced by the types of masterbatches.
Although the tensile and flexural moduli are different in the deformation mechanism (extension in tensile vs. bending in flexural testing), in sample geometry and dimensions (dogbone vs. bar-shaped), they are typically closely related when considering the elastic-range of stiffness of the materials. Thus, from this viewpoint, it is justified that the same overall trends were observed from both tensile and flexural moduli. Moreover, it was noticed that the tensile modulus was higher than the flexural modulus, when compared with the same nanocomposites and filler content (Appendix A), a fact that probably reflects mostly the faster deformation rate in the tensile experiments.

Finally, it is well-established that the mechanical properties depend also on the crystallinity of the polymer in unfilled form and in composites [107]. The correlation of the tensile modulus and the crystallinity of HDPE nanocomposites compared to the unfilled HDPEs are shown in Figure 5-15, 5-16, and 5-17, with XI40, YI40, and ZI40 based masterbatches, respectively, for all HDPE (A, C, and D). The change of crystallinity showed no definitive trend with the value of the tensile modulus at different clay contents. However, the comparison between the three types of masterbatches revealed that the XI40 and YI40 based masterbatches show less variation in the composite crystallinity, than that of ZI40 system.

Therefore, from our results, the tensile modulus enhancement from HDPE/organoclay nanocomposites cannot be attributed to the change of polymer crystallinity, but it is more likely to be due to the incorporation of the HDPE-g-MA bearing organoclay. This observation is in agreement with the findings reported elsewhere [131, 132].
Figure 5-15: Plot of tensile Young’s modulus versus crystallinity of all HDPE nanocomposites with XI40 based maserbatch compared to the respective unfilled HDPEs. The variation of the polymer crystallinity does not show a specific trend related to the tensile modulus enhancement.
Figure 5-16: Plot of tensile Young’s modulus versus crystallinity for all HDPE nanocomposites with Y140 based masterbatch compared to the respective unfilled HDPEs. The variation of the polymer crystallinity does not show a specific trend related to the tensile modulus enhancement.
Figure 5-17: Plot of tensile Young’s modulus versus crystallinity for all HDPE nanocomposites with ZI40 based masterbatch compared to the respective unfilled HDPEs. The variation of the polymer crystallinity does not show a specific trend related to the tensile modulus enhancement.
Finally, the presence of HDPE-g-MA in the polymer nanocomposites raises questions about the competition between any co-crystallization effect of the HDPE-g-MA and any reinforcing effect of the clay. Such a competition is definitely plausible and should be clarified. According to our previous studies on PP-based nanocomposites by Xu et al. [42], the best way to trace the origins of mechanical reinforcement for these nanocomposites is to correlate the tensile Young’s modulus to the crystallinity of polymer after taking into account the effect of the MA-polymer in absence of clay fillers. Thus, in order to compare the present results on HDPE, we prepared a series of HDPE/HDPE-g-MA blends (without clay), selecting HDPE-A and HDPE-g-MA-Z as representative materials and at the blend composition (specifically, we selected blend compositions that correspond to the two polymer ratios in the AxxZI40 nanocomposites with 1%, 6%, and 12 wt. % of clay). Thermal characterization and tensile testing were carried out: The tensile Young’s modulus of the blends was plotted versus the polymer crystallinity compared to that of the unfilled HDPE, and neat HDPE-g-MA. The plot shown in Figure 5-18 indicates that the Z polymer in AZ blends reduces not only the stiffness, but also the crystallinity of polymer. When the blends were compared with the nanocomposites, an enhancement of modulus was observed. Therefore, it is clarified that the modulus enhancement is derived from the incorporation of nano-fillers (clay) into the polymer matrix rather than that from the HDPE-g-MA as seen from the blends. In addition, the reduction of crystallinity by the HDPE-g-MA, a posteriori confirms our supposition that any heterogeneous nucleation effects of the mmt were masked by the presence of the functional polymer.
Figure 5-18: Plot of tensile Young’s modulus versus crystallinity for the unfilled “A”, neat “Z”, AZ blends, and the AZI40 nanocomposites. This comparison shows that the modulus enhancement is due to the organoclay inclusions, overwhelming the HDPE-g-MA ‘plasticization’ effect.

5.3.3.2 Injection Molding

A single-step process (Injection molding alone) was used to prepare selected HDPE nanocomposites by direct mixing of polymer and masterbatch pellets within the injection molder, without a prior extrusion involved for the masterbatch letdown. This approach is intended to emphasize any kinetic effects involved in the nanocomposite
formation of HDPE with HDPE-g-MA/organo-mmt masterbatch. The mechanical properties of the prepared composites were studied, and the results were compared with those of same formulation nanocomposites prepared through a two-step process (Extrusion letdown followed by Injection molding). The tensile properties, including relative tensile/Young’s modulus, relative tensile strength, and relative elongation at break are present in Figures 5-19, 5-20, 5-21, and 5-22 for AYI40, AZI40, CZI40, and DZI40 nanocomposites, respectively.

It was observed that for AYI40 nanocomposites, Figure 5-19, the difference in tensile modulus, and elongation at break were significant, especially at high clay content (6 wt.% inorganic). The processing method did not affect the tensile strength of these systems, as has been found with the rest of the prepared HDPE nanocomposites (AZI40, CZI40, and DZI40). For the nanocomposites with ZI40 based masterbatches, the tensile modulus, tensile strength, and elongation at break were in the same range for the samples prepared by single step and by the two-step process, CZI40 (Figure 5-21), except for the elongation at break at high clay loadings (which dramatically increased by 143% and 94% for C30ZI40 and C60ZI4, compared to the reduction by 35% and 8% for the two-step compounded samples).

The flexural properties, quantified through flexural modulus, flexural stress at yield, and flexural yield strain, did not show any significant difference when changing the processing method, as seen from Appendices A and B.

On the basis of the above findings, it might be possible to conclude that both methods allow to achieve nanocomposites with comparable mechanical properties. Explanation of the superior performance (viz. higher elongation at break) from the CZI40
nanocomposites, necessitate further structural and morphological investigation, but this is a minor point in the current research outlook. In all, it was shown that it may be possible that a single step process –direct injection molding of polymer and masterbatch– turn out to be an effective method for the preparation of these polymer nanocomposites.
Figure 5-19: Plot of relative Young’s modulus, relative tensile strength, and relative elongation at break of AY140 nanocomposites prepared from single and two-step process, compared to the unfilled “A”. The comparison of these two processes shows that the tensile properties are mostly unchanged, except the reduction of the elongation at break at high clay content.
Figure 5-20: Plot of relative Young’s modulus, relative tensile strength, and relative elongation at break of AZI40 nanocomposites prepared from a single and a two-step process; all properties are compared to the ones of the unfilled “A” HDPE. It is found that there is no significant effect of the processing method on the tensile properties.
Figure 5-21: Plot of relative Young’s modulus, relative tensile strength, and relative elongation at break of CZI40 nanocomposites prepared from single and two-step process, compared to the unfilled “C”. There is no significant effect of the processing to the tensile modulus and tensile strength, except dramatically increase elongation at break of the samples at 3% and 6 wt.% clay content.
Figure 5-22: Plot of relative Young’s modulus, relative tensile strength, and relative elongation at break of DZI40 nanocomposites prepared from a single and a two-step process; all values are compared to the ones from the unfilled “D” HDPE. It is found that there is no significant effect of the processing method on the tensile properties.
5.3.4 Mechanical Property and Antimicrobial activity of HDPE Reinforced with Two Organoclays (\textit{mmt}-DDOAB and \textit{mmt}-BDDAC) Nanocomposites

The objective of this part of the work is to combine two different organoclays, so as to simultaneously achieve mechanical performance, based on one of the organoclays, as well as antimicrobial functionality, based on the other organoclay. In particular, we focus on similar PE/organoclay nanocomposites (based on the study from Chapter 4), and here we reinforce with a ‘blend’ of two different organoclays, at a constant combined filler loading of 6 wt% inorganic.

It is well established that dialkyl ammonium surfactants with long alkyl chain (hexadecyl, octadecyl) can promote dispersion and improve mechanical property of PE nanocomposites, especially when aided by a functional-PE [56]. However, as demonstrated previously in this study, this same dialkyl surfactant (DDOAB) does not exhibit antifungal activity against the fungi tested. On the other hand, our efficient antifungal nanocomposite with BDDAC showed poorer dispersions and, accordingly, limited mechanical reinforcement. Thus, the idea of combining these properties by using a mixture of two organoclays, at an appropriate ratio may be advantageous to get simultaneous antifungal and higher mechanical performance PE nanocomposites.

The main parameter in this experimental design would be the relative ratio between \textit{mmt}-DDOAB and \textit{mmt}-BDDAC organoclay, under a constant total filler loading of 6 wt% \textit{mmt}. Generally, in order to get good dispersion and optimum mechanical reinforcement, 100% of DDOAB is used. On the other hand, for antimicrobial activity BDDAC should be used, which had high antifungal functionality even at extremely low concentrations. So, as a first approach, we will maintain the total concentration of
DDOAB plus BDDAC at the “high” 6 wt% inorganic (mmt) level, and will vary the relative amounts of the two organoclays, as shown in Table 5-4. Moreover, we used HDPE-A as a polymer matrix and Y, HDPE-g-MA as a polymeric compatibilizer in the master-batches for nanocomposite formation (both A and Y grades of HDPE and HDPE-g-MA, respectively, are the same commercially-available high-density PEs used before in this thesis).

This study involved dry-blending of two organo-clay powders at varied ratios (mmt-DDOAB and mmt-BDDAC) and subsequent preparation of HDPE nanocomposites at 6 wt% of clay content, via a masterbatch approach. Mechanical property and antimicrobial activity were investigated.

Table 5-4: The amount of clay in HDPE nanocomposites.

<table>
<thead>
<tr>
<th>Clay content in mmt-DDOAB</th>
<th>Clay content in mmt-BDDAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 1(mmt-DDOAB)</td>
<td>6</td>
</tr>
<tr>
<td>Sample 1</td>
<td>5</td>
</tr>
<tr>
<td>Sample 2</td>
<td>3</td>
</tr>
<tr>
<td>Sample 3</td>
<td>1</td>
</tr>
<tr>
<td>Control 2(mmt-BDDAC)</td>
<td>0</td>
</tr>
</tbody>
</table>

5.3.4.1 Mechanical Properties

Tensile properties of HDPE-A/organoclay nanocomposites were used as an indicator of the mechanical reinforcement, and specifically we report tensile performance of the nanocomposites compared to that of the unfilled HDPE-A, presented in Table 5-5.
The greatest tensile modulus enhancement is observed for the Control 1 sample, HDPE/mmt-DDOAB nanocomposite, as expected, since this filler is used to obtain mechanical reinforcement. Specifically, for this system, the modulus was increased by 30% compared to the unfilled HDPE. For the organoclay-blend nanocomposites (samples 1, 2, and 3), it was found that the modulus increased, almost linearly, with the amount of mmt-DDOAB. The lowest mechanical reinforcement was for the HDPE/mmt-BDDAC nanocomposite, again as expected since this filler was used to obtain antifungal activity rather than mechanical reinforcement. This means mmt-DDOAB disperses better in the HDPE polymer, compared to mmt-BDDAC, and it may further be implied that the improvement of tensile modulus in the organoclay blend system mainly originates from the mmt-DDOAB fillers alone, with mmt-BDDAC having a much smaller, if any at all, contribution. It is impossible to get a perfectly homogeneous dispersion by mixing mmt-DDOAB and mmt-BDDAC together, because the two organoclays have different polarity and thus different interactions with the polymer matrix. Also, there is probably some macroscopic phase separation within the composite with regions rich in mmt-BDDAC and regions poor in mmt-BDDAC, whereas mmt-DDOAB can disperse better in the polymer and it is expected to be located throughout the matrix where space is available (i.e., in less amounts where the other filler is at high local concentrations).
5.3.4.2 Antifungal Activity of HDPE/organoclay Blend Nanocomposites

The antifungal activity of the HDPE/organoclay blend (mmt-DDOAB and mmt-BDDAC) nanocomposites against *F.graminearum* and *P.roqueforti*, as representative fungi of a very robust (soilborne) and moderately robust (foodborne) organism, respectively. The antifungal activity was evaluated and compared to the unfilled HDPE, control 1 (a nanocomposite based on mmt-DDOAB), and control 2 (a nanocomposite based on mmt-BDDAC). Both qualitative and quantitative studies was carried out, as for the previous nanocomposite films before. The inoculated *F.graminearum* spores germinated on all films, while the degree of the growth was different depending on the ratio of mmt-DDOAB and mmt-BDDAC, as shown in Figure 5-23. From the morphological characterization, longer hyphal structures were observed for unfilled HDPE, control 1, and sample 1 (5:1 of mmt-DDOAB: mmt-BDDAC). By increasing the

<table>
<thead>
<tr>
<th></th>
<th>Tensile Modulus (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at Break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled HDPE</td>
<td>1232 ± 31</td>
<td>28 ± 0.3</td>
<td>298 ± 4</td>
</tr>
<tr>
<td>Control 1 (mmt-DDOAB)</td>
<td>1595 ± 42</td>
<td>31 ± 0.4</td>
<td>217 ± 18</td>
</tr>
<tr>
<td>Sample 1</td>
<td>1482 ± 39</td>
<td>30 ± 0.4</td>
<td>214 ± 30</td>
</tr>
<tr>
<td>Sample 2</td>
<td>1301 ± 35</td>
<td>29 ± 0.4</td>
<td>221 ± 14</td>
</tr>
<tr>
<td>Sample 3</td>
<td>1272 ± 39</td>
<td>29 ± 0.2</td>
<td>208 ± 21</td>
</tr>
<tr>
<td>Control 2 (mmt-BDDAC)</td>
<td>1261 ± 19</td>
<td>28 ± 0.7</td>
<td>256 ± 27</td>
</tr>
</tbody>
</table>

Table 5-5: Tensile properties of HDPE-A and HDPE-A/organoclay nanocomposites.
ratio of $mmt$-BDDAC in the films, the observed fungal growth became increasingly slower. The quantitative study (Table 5-6) presented that at 8 hours of post-inoculation, $F. graminearum$ spores germinated at 98% for PE and 97% for HDPE/$mmt$-DDOAB nanocomposite films. The percentage was reduced when $mmt$-BDDAC was added into the samples, replacing the $mmt$-DDOAB fillers.

For $P. roqueforti$, a similar trend to that of $F. graminearum$ was observed as shown in Figure 5-24. The spore germination was clearly observed on unfilled HDPE, HDPE/$mmt$-DDOAB, and HDPE/$mmt$-DDOAB/$mmt$-BDDAC at the clay ratio to 5:1. At the ratio of 3:3, very short germinated tubes were observed, and those only at higher magnification (400x), Figure 5-25. The quantitative analysis is shown in Table 5-6, which suggests that a growth inhibition at high ratio of $mmt$-BDDAC in HDPE nanocomposites. These results indicate that the concentration of BDDAC in the sample is an important factor that controls the fungal growth, and this is in excellent agreement with the observations from the previous study (Chapter 4).
Figure 5-23: Optical micrographs of the growth development of *F. graminearum* spores on unfilled PE, control 1, sample 1, sample 2, sample 3, and control 2 nanocomposite films. These illustrate the growth after 8 hours of inoculation of $2 \times 10^5$ spores/ml at 200x magnification.
Figure 5-24: Optical micrographs of the growth development of *P. roaueforti* spores on unfilled PE, control 1, sample 1, sample 2, sample 3, and control 2 nanocomposite films. These illustrate the growth after 24 hours of inoculation of $2 \times 10^5$ spores/ml at 200x magnification.
Figure 5-25: Optical micrographs of the growth development of *P. roqueforti* spores on HDPE/(3:3 *mmt*-DDOAB : *mmt*-BDDAC) nanocomposite films. This illustrates the growth after 24 hours of inoculation of $2 \times 10^5$ spores/ml at 400x magnification.

Table 5-6: Percentage of spore germination on the PE and PE nanocomposite films.

<table>
<thead>
<tr>
<th>Fungi</th>
<th>Control PE (unfilled)</th>
<th>PE / 6 wt% clay nanocomposite (<em>mmt</em>-DDOAB : <em>mmt</em>-BDDAC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>6:0</td>
</tr>
<tr>
<td><em>F. graminearum</em></td>
<td>Time (h)</td>
<td>Spore Germination (%)</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>98</td>
</tr>
<tr>
<td><em>P. roqueforti</em></td>
<td>24</td>
<td>10</td>
</tr>
</tbody>
</table>
5.4 Summary

In this Chapter, HDPE/organoclay nanocomposites were prepared by masterbatches using three HDPE matrices, and three compatibilizers (HDPE-g-MAs), all of which differed in their Mw, density, and crystallinity. The composites’ structures, thermal properties, and mechanical properties were investigated. A promising appropriate HDPE/HDPE-g-MA pairing was identified, by comparing their mechanical performance and crystallinity changes. It was found that lower than the matrix Mw HDPE-g-MA (Y) better enhanced the tensile properties of all HDPEs (A, C, and D) compared to that of higher Mw HDPE-g-MAs (X and Z). The flexural properties markedly unaffected by this parameter, and only showed the expected dependence on the amount of clay. In addition, the high molecular weight HDPE-C showed significant improvement in the tensile modulus, while the lower molecular weight HDPE-A, and -D showed smaller increases only.

From the thermal characterization, the HDPE nanocomposites were found to show no major change in crystallization behavior upon nanocomposite formation. The unchanged $T_c$ (heterogeneous nucleation by mmt balances any plasticization effects from the HDPE-g-MA) denoted an uncommon behavior for polyolefin/clay nanocomposites. The small change of crystallinity found between all prepared nanocomposites, showed better performance from the X and Y grades of HDPE-g-MA compared to the Z grade (greater change of crystallinity).

Moreover, it was shown that the modulus enhancement originates from the incorporation of nanofillers (clays) into the polymer matrix, which evidently overwhelms
any ‘negative’ effects from the HDPE-g-MA, as seen from comparing the nanocomposites against the respective HDPE/HDPE-g-MA blends (no fillers).

Additionally, this present study has demonstrated that for the systems studied here it is possible to obtain polymer nanocomposites by melt blending applying through a single-step low-mixing-ability processing (direct injection molding of the polymer and the masterbatch). The mechanical properties of such prepared nanocomposites were determined and compared to that of same formulation samples prepared by the standard two-step process (extrusion for letdown followed by injection molding). It was shown that the preparation method did not markedly affect either the tensile or the flexural properties of the nanocomposites. Based on the comparable mechanical properties, it may be concluded that using a single-step process is appropriate for preparing such polymer nanocomposites, where the thermodynamics of mixing are strong enough and can overcome changes in the processing conditions that would otherwise lead to poor filler dispersions and, thus, poor performing nanocomposites. However, further work of structural and morphological characterization should be carried out to completely explain the one change observed in the elongation-at-break of the higher Mw HDPE.
Chapter 6

Polymer/LDH Nanocomposites: Morphology and Dispersion

6.1 Introduction

Polymer/clay nanocomposites have received an intense interest after the pioneering work on nylon6/mmt systems which revealed the formation of nanostructured composite materials with multiple, concurrent, non-trivial property improvements, including thermo-mechanical properties, gas barrier performance, and thermal properties [6, 7, 133]. By now, the field is rather mature, and the majority of commercial applications and of numerous research studies has typically focused on the mica-type 2:1 alumino-silicates (especially cationic clays). More recent research has been expanding into other types of layered materials, like layered double hydroxides (LDHs), commonly called anionic clays, as an alternative and possibly more advantageous layered material for the preparation of multifunctional polymer/clay nanocomposites [134]. Because of the highly tunable properties of LDHs, these nanocomposites possess potential towards improving specific applications, such as electrical, luminescence [10], photo/UV stability [11], antimicrobial activity [12], and especially flame retardancy. The last application is being extensively investigated through the use of LDH nanofillers as potential non-halogenated fire retardant (FR) additives for polymers. Towards this end, organically modified LDH layers have been dispersed in various polymers, such as poly(methyl methacrylate) (PMMA) [135], low-density polyethylene (LDPE) [136], polyamide (PA) [137], polystyrene (PS) [138], and epoxy [139].
In this chapter, we primarily present our studies, which were a part of a collaborative research with other groups specializing in inorganic synthesis and fire research, and we only focus on our work in LDH-based polymer composite materials. Specifically, we investigated the compatibility of the LDHs with polar and non-polar polymers, including PMMA, PS, PE, and PP, and we systematically investigated the morphology and dispersion of the LDHs in these polymers, at the micrometer and the nanometer length-scales. The details related to the synthesis of the LDHs and the fire retardancy studies of the nanocomposites, were carried out elsewhere and are not discussed here; however, these are presented in the following publications:


6.2 Experimental Section

6.2.1 Materials

All polymers used in these studies were commercially available grades. Specifically, commercial polymers, poly(methyl methacrylate) (PMMA, \( M_w \) 120000), polystyrene (PS, \( M_w \sim 230000, M_n \sim 140000 \)), low density polyethylene (PE, density 0.920g/cm\(^3\) and melt flow rate 1g/10min (190°C/2.16kg), and polypropylene (PP, Petrothene PP 31KK01) were used in the studies.

6.2.2 Preparation of LDH

The co-precipitation method was used to synthesize LDHs and the organic modification was done through the ion-exchange reaction or co-precipitation method. The synthesis and modification procedures are not presented in this chapter, however, the details can be found in the publication listed above (paragraph 6.1).

6.2.3 Nanocomposite Preparation

The polymers used to prepare polymer/LDHs nanocomposites are PMMA, PS, PE, and PP. The polymer nanocomposites, including PMMA, PE, and PP, were prepared via melt blending process in a Brabender Plasticorder twin-head kneader at a screw speed of 60 rpm at the various temperatures and residence times shown in Table 6-1. The PS nanocomposites were prepared via bulk polymerization of styrene monomer (99%) [140].
Table 6-1: Materials and processing conditions.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>LDH</th>
<th>Surfactant</th>
<th>Preparation method</th>
<th>Processing temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>MgAl-LDH</td>
<td>Linear alkyl carboxylate</td>
<td>Melt blending</td>
<td>185</td>
</tr>
<tr>
<td>PMMA</td>
<td>MgAl-LDH, ZnAl-LDH</td>
<td>Oleate anion</td>
<td>Melt blending</td>
<td>185</td>
</tr>
<tr>
<td>PS</td>
<td>MgAl-LDH</td>
<td>Linear alkyl carboxylate</td>
<td>Bulk polymerization</td>
<td>-</td>
</tr>
<tr>
<td>PE</td>
<td>MgAl-LDH, ZnAl-LDH</td>
<td>Oleate anion</td>
<td>Melt blending</td>
<td>140</td>
</tr>
<tr>
<td>PP</td>
<td>MgAl-LDH, ZnAl-LDH</td>
<td>Oleate anion</td>
<td>Melt blending</td>
<td>180</td>
</tr>
</tbody>
</table>

6.2.4 Structural Characterization

In order to study the morphology and dispersion of these LDHs in the polymer nanocomposites, X-ray diffraction (XRD) and Transmission electron microscopy (TEM) were used. Focusing on the TEM characterization, bright-field transmission electron microscope (TEM) images of the samples were obtained with a JEOL 1200 EXII transmission microscope operated at an accelerating voltage of 80 kV, and equipped with a Tietz F224 digital camera (Penn State Life Sciences EM facilities). Ultrathin sections (70–100 nm) of the nanocomposites were obtained from cryogenically cutting with an ultramicrotome (Leica Ultracut UCT) equipped with a diamond knife. The sections were transferred to carbon-coated copper grids (200-mesh, with a Lacey support film). No
heavy metal staining of sections prior to imaging was done, since the contrast between the fillers and the polymer matrix was sufficient.

6.3 Results and Discussion

The morphology and dispersion of LDH in various polymers were investigated by using transmission electron microscopy (TEM). The TEM images at low magnification are used to determine the overall dispersion of the layered material in the polymer at the micrometer length-scale (tactoids and agglomerate observation), while the higher magnification images provide more detail on the nanometer scale dispersion (e.g. intercalated or exfoliated morphologies). Alkyl carboxylate-modified MgAl-LDHs were prepared and used as nano-fillers for PMMA and PS, representative of polymers with rather different polar interactions. The LDH was first intercalated with linear alkyl carboxylates (CH$_3$(CH$_2$)$_n$COO$, n = 8, 10, 12, 14, 16, and 20) via anionic exchange of MgAl-nitrates. MgAl-undecenoate LDH was prepared by the co-precipitation method. The MgAl-LDHs were melt-blended with PMMA and bulk polymerized with styrene to form the nanocomposites.

The nanocomposite structure was obtained from direct observation of the LDH dispersion and typical TEM images are present in Figure 6-1 for some of the PMMA/LDH systems (C10, C16, and C18) and the TEM images from the remaining systems are in Figure 6-2. The MgAl-C10 layers are mostly isolated and uniformly dispersed in PMMA at low magnification. There may also been some small tactoids present. At higher magnification, the MgAl-C10 layers are not parallel. The
intercalation was also confirmed by TEM for MgAl-C12, MgAl-C14, MgAl-C16, MgAl-C18, and MgAl-C22 PMMA nanocomposites.

All of the carboxylates with alkyls longer than C10 show evidence of intercalation and, in many instances, e.g., C12, C14, and C16, show clay layers both in and out of parallel registry, \textit{i.e.}, both intercalated and exfoliated layers are coexisting in the composite. For C18 and C22, only layers in parallel registry can be seen. The best descriptions of the nanocomposite morphology are: C10, exfoliated; C12, C14, C16, mixed intercalated-exfoliated; C18 and C22, intercalated.

These clearly show good nanodispersion and the presence of either individual clay platelets or, at worst, a small number of platelets together. These PMMA/LDH systems are all ‘true’ nanocomposites and their morphologies should probably be described as mixed intercalated-exfoliated.
Figure 6-1: TEM images at (a) low and (b) high magnification for PMMA + 3% MgAl-C10, (c) low and (d) high magnification for PMMA + 3% MgAl-C16, and (e) low and (d) high magnification for PMMA + 3% MgAl-C18. The scale bars are indicated on the images.
Figure 6-2: TEM images at (a) low and (b) high magnification for PMMA+3%MgAl-C12, (c) low and (d) high magnification for PMMA+3%MgAl-C14, and (e) low and (f) high magnification for PMMA+3%MgAl-C22. The scale bars for low and high magnification are indicated on the images.
The TEM images for the PS/MgAl-C11 LDH composite are presented in Figure 6-3, while the structure of the C22 composite is shown in Figure 6-4. The TEM images for PS/LDH composites (C10 to C18) are presented in Figure 6-5. The PS/MgAl-C11 composites show a qualitatively different dispersion than the PS composites based on alkyl carboxylate (C10-C22) modified MgAl. Specifically, at the micrometer scale, the MgAl-C11 shows a substantially better swelling of the agglomerates by PS, with most of the tactoids being delaminated down to individual layers or highly-disordered well-dispersed groups of a few layers (nanometer scale). Very few tactoids, typically composed of the larger lateral-dimension LDH layers, retain their parallel registry (intercalated tactoid structures). This carboxylate contains a terminal double bond, which may have participated in the polymerization and thus could have led to better LDH nano-dispersion. This has also been seen with mmt systems. For the composites based on saturated alkyl-exchanged MgAl LDHs (Figure 6-4), the dispersion at the nano-scale level is similar to PS/mmt systems. At the micrometer scale, the MgAl LDHs show definitive agglomeration (moderate to poor dispersion) characteristic of the “conventional composite”/microcomposite structures of typical polystyrene/LDH composites. However, they show good dispersions at the nanoscale, with individual LDH layers being separated by polystyrene, forming intercalated or disorderly swollen tactoids of LDH layers (Figure 6-4 and Figure 6-5). The extent/tendency of PS intercalation between the organically modified LDH seems to be increasing with longer alkyl lengths of the carboxylates, in good agreement with thermodynamic considerations of polymer/organo-clay mixing. This is because the LDH becomes more organophillic with longer organic modifications and thus more compatible with the polymer. This dispersion improvement
with the length of the alkyl-anion in the LDH, is also reflected in better swelling of the agglomerates by PS at the micrometer scale, considering the swelling of the LDH agglomerates, however, all the composites show substantial agglomeration and can be assigned as microcomposites. Only for the longest organic modifications (PS/MgAl-C22) was the presence of a few isolated/exfoliated LDH layers in the polymer observed.

Figure 6-3: The structure of the PS composite reinforced by the 10-undecenoic acid modified MgAl (cf. MgAl-C11), by bright-field imaging.
Figure 6-4: Hierarchical structure of the PS composites with linear alkyl carboxylate (C10-C20)-modified MgAl, as exemplified by bright-field TEM imaging of the structure of MgAl-C22 at various magnification.
Figure 6-5: …(continues on next page)
Figure 6-5: TEM images at (a) low and (b) high magnification for PS + 3% MgAl-C10, (c) low and (d) high magnification for PS + 3% MgAl-C12, (e) low and (f) high magnification for PS + 3% MgAl-C14, and (g) low and (h) high magnification for PS + 3% MgAl-C16. The scale bars are indicated on the images.
The effect of LDH divalent metals on the composite morphology and dispersion was also studied, by comparing ZnAl-LDHs and MgAl-LDHs as nano-fillers for the same PE and PMMA matrices. Oleate anion (CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_7$COO-) was used to modify both types of LDH. This anion was preferred to other possible surfactants because of its excellent combination of high thermal stability, good water solubility, and relatively low cost [141]. A melt-blending process in a twin-head kneader was used to prepare both PE/LDH and PMMA/LDH systems, under the same processing conditions. There are differences in the shape and size of the LDH when comparing between ZnAl and MgAl, primarily because co-precipitated zinc aluminum oleate typically shows structures quite different from the regular hexagonal platy sheets (e.g. MnAl tactoids) often containing small irregular particles [142] (vide infra).

The dispersion of the LDH in PE is presented in Figure 6-6 of PE/3% MgAl (Figure 6-6 A) and PE/3% ZnAl (Figure 6-6 B). The lower magnification images for both LDHs in PE shows relatively poor dispersions, with sub-micrometer tactoids (agglomeration of LDHs) observed for both systems, ZnAl seems better dispersed in PE than is MgAl. The composite morphology can probably be described as intercalated with disordering for PE/3% ZnAl, while a microcomposite (no nanoscale filler dispersion) is probably formed in the case of PE/3% MgAl.
Figure 6-6: The structure of the PE/3% MgAl oleate LDH (A1, A2), and PE/3% ZnAl oleate LDH (B1, B2) by bright-field imaging.
The composite morphology is qualitatively different for the PMMA-based composites. Figure 6-7 shows the TEM images of PMMA containing 3 wt.% MgAl (Figure 6-7 A1, A2) and 3 wt.% ZnAl (Figure 6-7 B1, B2). The lower magnification images of both systems show relatively good dispersion, with only a few tactoids observed for the ZnAl-containing PMMA/LDH system, and these are much smaller in size than those in the PE composites. Comparison of the two PMMA composites indicates better dispersion of MgAl oleate than of the ZnAl oleate. This trend in dispersion is opposite to what is seen for the PE systems, where ZnAl shows better dispersion than MgAl.

All TEM images indicate that the ZnAl have smaller particle sizes than typically seen in LDHs. This is in agreement with previous work [142], where it was reported that co-precipitated zinc aluminum oleate showed structures quite different from the regular hexagonal platy sheets (tactoids) containing small irregular particles [142]. In order to confirm that this is also the case here for MgAl, and also to confirm that the thickness of the microtomed specimens is not a factor, we extracted the particles from the PMMA composite and observed them with TEM. Namely, PMMA/3% MgAl was dissolved in acetone, and the solution was left to stand for 3 days before collecting the precipitant from the bottom of the vial, and cast on a lace-coated TEM grid. Figure 6-8 shows images of these extracted particles. The LDH particle size is small, about 10-20 nm long. Individual layers are observed, and also stacks of 2-5 layers are seen. It is significant to note that small stacks and individual platelets all had relatively low aspect ratios LDHs layers (typical length of about 20 nm).
Figure 6-7: The structure of the PMMA/3% MgAl oleate LDH (A1, A2), and PMMA/3% ZnAl oleate LDH (B1, B2) by TEM.
Figure 6-8: TEM images of MgAl extracted from PMMA/3% MgAl with acetone.
The oleate-containing LDHs with zinc and magnesium based compositions were also used to prepare nanocomposites of polypropylene (PP) via melt blending process. The influence of LDH composition and of the presence and amount of a polymeric compatibilizer --PP-g-MA in this case-- in the dispersion of PP/LDH system were investigated.

From the TEM images of PP/PP-g-MA (1:1)/4% MgAl-LDH (Figure 6-9), the observed structures can be described as a mixed intercalated/exfoliated morphology, with most of the LDH layers being well-dispersed and disordered. The LDH tactoids, with typical sizes 50-150 nm, are swollen by polymer. The PP/PP-g-MA (1:1)/4% ZnAl-LDH composites also show a mixed intercalated/exfoliated structure, with the LDH layers mostly well-dispersed. The LDH tactoids show much smaller sizes than the tactoids in the PP/PP-g-MA (1:1)/4% MgAl-LDH, and are typically 10-30 nm with very few larger ones (at 50-150nm), while the larger scale agglomerates are very-highly swollen by polymer (PP and PP-g-MA). Comparing the PP/PP-g-MA (1:1)/4% MgAl-LDH and the PP/PP-g-MA (1:1)/4% ZnAl-LDH morphologies, the filler dispersions at the nanometer scale is more-or-less the same, while at the micrometer scale the PP/PP-g-MA (1:1)/4% ZnAl-LDH seems better dispersed than the PP/PP-g-MA (1:1)/4% MgAl-LDH. This last is probably due to differences in the LDH layer sizes, with ZnAl being substantially smaller than MgAl in lateral dimensions and, consequently, leading to an easier dispersion of the corresponding agglomerates in PP/PP-g-MA (1:1) [compared to the ones in the PP/PP-g-MA (1:1)/4% MgAl-LDH].

TEM images on a sample of PP/ ZnAl-LDH that contains a smaller content of PP-g-MA were also obtained and compared with the previous two samples with higher
PP-g-MA content. The structure of PP/PP-g-MA (8:1)/4% ZnAl-LDH is also a mixed intercalated/exfoliated structure, but this sample contains well-defined agglomerates, 200–500 nm in size, and, within these the LDH tactoids seem intercalated and are separated by many disordered LDH layers between these tactoids. These disordered layers seem less dispersed, of higher density and with smaller layer to layer separations, than those in the PP/PP-g-MA (1:1)/4% ZnAl-LDH. Comparing PP/PP-g-MA (8:1)/4% ZnAl-LDH and PP/PP-g-MA (1:1)/4% ZnAl-LDH, the dispersion of the system with more PP-g-MA seems slightly better both at the nanometer and at the micrometer scales, in concert with the dispersion obtained by much larger montmorillonite silicates predispersed in PP-g-MA before dilution by unmodified PP [45]. Overall, the TEM studies reveal good dispersion, considering the high additive loadings investigated [4% AA= 15.4% MgAl-oleate (wt.%), while 4% AE = 11.1% ZnAl-oleate (wt.%)].
Figure 6-9: The TEM images of PP:PP-g-MA (1:1) 4% MgAl-oleate (A1, A2, A3), PP:PP-g-MA (1:1) 4% ZnAl-oleate (B1, B2, B3) and PP:PP-g-MA (8:1) 4% ZnAl-oleate (C1, C2, C3) at different magnifications.
6.4 Summary

The dispersion of organically modified LDHs in various polymers was investigated by transmission electron microscopy (TEM). The same melt blending process was used to prepare LDH in PMMA, PE, and PP systems, while bulk polymerization was used to prepare LDH/PS system.

From these studies, the dispersion of LDHs (composite morphology) in polymeric materials seems to be controlled by various important parameters. For polar polymers like PMMA, ‘true’ nanocomposite systems were observed because of the high compatibility between the LDH and the polymer. For PS composites, poorly-dispersed MgAl-LDHs (microcomposites) were observed. However, the surfactant structure could be manipulated to lead to better LDH nano-dispersions; for example, in one case a carboxylate which contained a terminal double bond, which can participate in the styrene polymerization, led to a much better dispersion than the saturated bond modifiers. Additionally, the extent of PS intercalation seems to be increasing with longer alkyl chain length of the carboxylates since the gallery space becomes more organophillic and thus more compatible with the polymer. This trend is opposite in case of LDH/PMMA systems, since the longer alkyls here effectively decrease the polar polymer-LDH interactions that drive dispersion.

More importantly, the type of divalent metal ion in oleate-containing LDH markedly affect the dispersion in different polymers. Both Mg- and Zn- based LDHs in PE shows relatively poor dispersion, with sub-micrometer tactoids (agglomeration of LDHs). However, the smaller ZnAl seems better dispersed in PE than is MgAl, as would
be expected from simple entropic considerations. Comparison of the two LDHs in PMMA composites indicates better dispersion of MgAl oleate than of the ZnAl oleate. This trend in dispersion is opposite to what is seen for the PE systems, again due to the fact that in the case of PMMA dispersion is driven by polar interactions. The size of oleate-modified LDH dispersed in PMMA is much smaller than those on the PE composites and carboxylate-modified PMMA.

For PP composites, the zinc containing LDH showed better dispersion at the micrometer level than did the magnesium-containing LDH, while both are equally well-dispersed at the nanometer level. Dispersion was also affected by the amount of PP-g-MA which was present, with more PP-g-MA gave better dispersion.
Chapter 7

Conclusions and Suggestions for Future Work

Important results and observations from this study regarding antimicrobial activity, optimization of mechanical properties, and dispersion of layered materials/polymer nanocomposites are summarized and the possible future work is suggested.

7.1 Conclusions

7.1.1 Antimicrobial Activity of Free Surfactant, their Organoclays, and LLDPE/LDPE Blend/Organoclay Nanocomposites

It is clearly observed that for the cationic surfactants with antifungal activity, the important factors that controlled the activity were primarily the chemical characteristics of the surfactants (activity also depended on fungal species tested), Chapter3. The charge of head group and the counter anion (i.e. amine, ammonium, and bromide ions) did not seem to play a role in the antifungal activity of this study. Moreover, pristine/unmodified clay (Na\(^+\)-mmt) was not directly responsible for the inhibitory activity.

Impressively, the high activity surfactants still maintained their antifungal property even when tethered onto clay particles (limiting surfactant transport).

More impressively, even as the fillers in the LLDPE/LDPE blend nanocomposite films, they still maintained the activity against the *Penicillium* spp (Chapter4). It seems the amount of organoclay is one of the important parameters to control the activity.
However, the activity against different fungal species was differently promoted. For the insusceptible fungus, *F. graminearum*, these potent surfactants presented small activity only at the early stage of germination based on the quantitative study.

### 7.1.2 Optimization of HDPE/I.44P Organoclay Nanocomposites’ Mechanical Properties

This study revealed that the low Mw compatibilizer, HDPE-g-MA, better enhanced the *tensile properties* of all HDPEs than that of high viscosity HDPE-g-MA. The *flexural properties* were not affected by this parameter, but were controlled by the amount of clay. In addition, the high molecular weight HDPE showed significant improvement in the tensile modulus, while the lower molecular weight HDPE showed small increases only. The nanocomposite formation did not present major effect to the crystallization behavior. The small change of crystallinity was found in all prepared nanocomposites depending on selected HDPE-g-MA. The X, and Y based masterbatch systems were more appropriate than Z (greater change of crystallinity).

Moreover, it is clarified that the modulus enhancement is derived from the incorporation of nano-fillers (clay) into the polymer matrix rather than that from the HDPE-g-MA as seen from the HDPE/HDPE-g-MA blend study.

Additionally, the present study has demonstrated the possibility to obtain polymer nanocomposites by melt blending applying single step process (injection molding). Their mechanical properties were determined and compared to that of the samples prepared by two-step process (extrusion and injection molding). It was evidenced that the preparation methods did not substantially affect both tensile and flexural properties of the
nanocomposites, except the high molecular weight polymer sample at 3%, and 6 wt. % of clay loading, in which the elongation at break dramatically increased. Based on the comparable mechanical properties, it may conclude that using single step process will be possible to prepare polymer nanocomposites. However, further work of structural and morphological characterization of high Mw samples may be suggested.

7.1.3 Mechanical Property and Antimicrobial Activity of HDPE/Organoclay Blend (mmt-DDOAB and mmt-BDDAC) Nanocomposites

The HDPE/organoclay blend nanocomposite was prepared by using two organoclays which enhance the dispersion and mechanical properties and possess high antimicrobial activity. The greatest reinforcement was observed for HDPE/mmt-DDOAB nanocomposites. It was found that by incorporating this mixture into HDPE, the tensile modulus increased with the ratio of mmt-DDOAB in the blend increased. Mmt-BDDAC seems not to well disperse in HDPE and presented small tensile modulus improvement. Blending of two organoclays seems not to promote homogeneous dispersion system. The more favorable organoclay (mmt-DDOAB) is better dispersed in the polymer than the lesser favorable one (mmt-BDDAC).

The antimicrobial activity originated from mmt-BDDAC still maintained at high ratio in the HDPE/organoclay blend nanocomposites.
7.1.4 Dispersion of LDH in various Polymer Nanocomposites

The dispersion and morphology of organically modified LDHs in various polymers were investigated by transmission electron microscopy (TEM). The melt blending process was used to prepare LDH in PMMA, PE, and PP systems, while the bulk polymerization was used to prepare LDH/PS system.

From these studies, the dispersion and morphology of LDHs in polymeric materials are controlled by various important parameters. For polar polymer like PMMA, the true nanocomposite systems were observed because of the high compatibility between the LDH and the polymer. For PS composites, poorly-dispersed MgAl-LDHs (microcomposites) was observed. However, the surfactant structure, in this case the carboxylate, which contains a terminal double bond may have participated in the polymerization and thus could have led to better LDH nano-dispersion than the saturated bond modifier. Additionally, the extent of PS intercalation seems to be increasing with longer alkyl chain length of the carboxylates since the gallery space becomes more organophillic and thus more compatible with the polymer. This trend is opposite in case of LDH/PMMA systems.

Moreover, the types of divalent metal ion in oleate-containing LDH differently affect the dispersion in different polymers. Both Mg- and Zn- based LDHs in PE shows relatively poor dispersion, with sub-micrometer tactoids (agglomeration of LDHs). However, the ZnAl seems better dispersed in PE than is MgAl. Comparison of the two PMMA composites indicates better dispersion of MgAl oleate than of the ZnAl oleate. This trend in dispersion is opposite to what is seen for the PE systems. The size of
oleate-modified LDH dispersed in PMMA is much smaller than those on the PE composites and carboxylate-modified PMMA.

For PP composites, the zinc containing LDH showed better dispersion at the micrometer level than did the magnesium-containing LDH while both are equally well-dispersed at the nanometer level. Dispersion was also affected by the amount of PP-g-MA which was present. More PP-g-MA gave better dispersion.

7.2 Suggestions for Future Work

7.2.1 Antimicrobial Mechanism of Surfactants

The mode of action of the antimicrobial cationic surfactants, such as quaternary ammonium compounds, has been identified. The proposed mechanism was presented by a specific role of positive charge and alkyl chain. However, the possible activities of the organic pendant group, such as benzyl functional group in BDDAC are thought to give better understanding. The benzyl-containing molecule promoted greater antifungal activity than the regular alkyl ammonium. The reactivity of this group could be investigated in future study.

Moreover, the non-ionic surfactant, PEDPA, which possess ethylene oxide group, may have different binding sites and may act in distinct ways from the cationic surfactants. The arrangement of such structure may be more complex than the simple disruption to the cell. The model system explaining its reactivity should be proved in future studies.
7.2.2 Combine Mechanical Property and Antimicrobial Activity by Modifying Clay with a Mixture of Two Surfactants

According to study in Chapter 5, we attempted to improve the dispersion of clay and simultaneously achieve mechanical performance as well as maintain antimicrobial activity of the PE/organoclay nanocomposites by using two different organoclays. It was found that using the blend of two organoclays led only to limited mechanical reinforcement. Thus, the idea of combining these properties by using a mixture of two surfactants, at an appropriate ratio, to modify mmt may be advantageous to get simultaneous antifungal and high mechanical performance PE nanocomposites.

The main parameter in this experimental design would be the ratio between DDOAB and BDDAC surfactant in the organoclay.

Dispersion of organoclay in polymer matrix (XRD and TEM), thermomechanical property (DSC, tensile and flexural), and antimicrobial activity should be investigated and compared to the blend of two organoclay systems.

7.2.3 Multifunctional Polymer Nanocomposites

Multifunctional viewpoint of polymer nanocomposites will be crucial in material development. Polymer blending is an attractive idea to produce new materials promoted synergism among the polymer pairs with targeted multi-properties with respect to those of the parent components. Blends of polyolefins, such as polyethylene (PE) with polyamides are particularly interesting because of the good processability and toughness of the former with excellent mechanical properties of the latter [143]. Based on our
study, the organoclay possesses high antimicrobial activity presented poor dispersion in PE. So by adding polyamide, the dispersion may be improved and the polymer blend nanocomposites would also exhibit good barrier against oxygen [144]. The multifunctional nano-materials with enhanced antimicrobial activity, mechanical properties, and high barrier property could be tailored in future studies.

7.2.4 LDH with Antimicrobial Functionality

Beside the flame retardant property of LDHs, new functionality, such as an antimicrobial material may be interesting. Based on highly tunable properties of LDH, ease of synthesizing, and their anion exchange capacity, LDH becomes one of the attractive candidates. Recently, it has been reported that benzoate and benzoate derivative anion with their antimicrobial activity were used to modify LDH and incorporated in polymer composites [12]. By selecting the appropriate active molecular anions, nanocomposites could be tailored for future antimicrobials material research.
REFERENCES


126. Xu, J.T., Q. Wang, and Z.Q. Fan, *Non-isothermal crystallization kinetics of exfoliated and intercalated polyethylene/montmorillonite nanocomposites*


### Mechanical Properties of HDPEs and HDPE/organoclay nanocomposites
(Two-Step Process)

#### Table A-1: Tensile properties of HDPE-A and HDPE-A/XI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1375 ± 40</td>
<td>32 ± 0.3</td>
<td>267 ± 13</td>
</tr>
<tr>
<td>A02XI40</td>
<td>1401 ± 54</td>
<td>32 ± 1</td>
<td>264 ± 8</td>
</tr>
<tr>
<td>A05XI40</td>
<td>1463 ± 54</td>
<td>34 ± 0.3</td>
<td>237 ± 50</td>
</tr>
<tr>
<td>A10XI40</td>
<td>1467 ± 38</td>
<td>33 ± 0.4</td>
<td>264 ± 12</td>
</tr>
<tr>
<td>A30XI40</td>
<td>1616 ± 56</td>
<td>36 ± 1</td>
<td>206 ± 58</td>
</tr>
<tr>
<td>A60XI40</td>
<td>1658 ± 68</td>
<td>37 ± 0.2</td>
<td>102 ± 17</td>
</tr>
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</table>

#### Table A-2: Flexural properties of HDPE-A and HDPE-A/XI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural modulus (MPa)</th>
<th>Flexural stress at yield (MPa)</th>
<th>Flexural strain at yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1095 ± 32</td>
<td>31 ± 0.4</td>
<td>7 ± 0.1</td>
</tr>
<tr>
<td>A02XI40</td>
<td>1112 ± 38</td>
<td>31 ± 0.1</td>
<td>8 ± 0.1</td>
</tr>
<tr>
<td>A05XI40</td>
<td>1157 ± 38</td>
<td>31 ± 0.2</td>
<td>8 ± 0.1</td>
</tr>
<tr>
<td>A10XI40</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>A30XI40</td>
<td>1260 ± 40</td>
<td>33 ± 0.04</td>
<td>8 ± 0.02</td>
</tr>
<tr>
<td>A60XI40</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
### Table A-3: Tensile properties of HDPE-C and HDPE-C/XI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
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<tbody>
<tr>
<td>C</td>
<td>625 ± 33</td>
<td>26 ± 1</td>
<td>146 ± 8</td>
</tr>
<tr>
<td>C02XI40</td>
<td>637 ± 32</td>
<td>24 ± 1</td>
<td>144 ± 14</td>
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<td>C05XI40</td>
<td>639 ± 52</td>
<td>24 ± 0.2</td>
<td>117 ± 8</td>
</tr>
<tr>
<td>C10XI40</td>
<td>650 ± 57</td>
<td>24 ± 1</td>
<td>118 ± 11</td>
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<tr>
<td>C30XI40</td>
<td>759 ± 48</td>
<td>26 ± 1</td>
<td>101 ± 6</td>
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<td>C60XI40</td>
<td>1143 ± 47</td>
<td>29 ± 1</td>
<td>174 ± 26</td>
</tr>
</tbody>
</table>

### Table A-4: Flexural properties of HDPE-C and HDPE-C/XI40 nanocomposites.

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<tr>
<th>Sample</th>
<th>Flexural modulus (MPa)</th>
<th>Flexural stress at yield (MPa)</th>
<th>Flexural strain at yield (%)</th>
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<tr>
<td>C</td>
<td>520 ± 10</td>
<td>19 ± 0.3</td>
<td>9 ± 0.3</td>
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<tr>
<td>C02XI40</td>
<td>530 ± 8</td>
<td>19 ± 0.1</td>
<td>9 ± 0.3</td>
</tr>
<tr>
<td>C05XI40</td>
<td>551 ± 8</td>
<td>20 ± 0.1</td>
<td>8 ± 0.2</td>
</tr>
<tr>
<td>C10XI40</td>
<td>577 ± 5</td>
<td>20 ± 0.1</td>
<td>9 ± 0.1</td>
</tr>
<tr>
<td>C30XI40</td>
<td>729 ± 12</td>
<td>22 ± 0.1</td>
<td>8 ± 0.1</td>
</tr>
<tr>
<td>C60XI40</td>
<td>1015 ± 18</td>
<td>25 ± 0.4</td>
<td>9 ± 0.1</td>
</tr>
</tbody>
</table>
### Table A-5: Tensile properties of HDPE-D and HDPE-D/XI40 nanocomposites.

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<tr>
<th>Sample</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
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<td>33 ± 1</td>
<td>87 ± 19</td>
</tr>
<tr>
<td>D02XI40</td>
<td>1552 ± 38</td>
<td>33 ± 0.1</td>
<td>68 ± 9</td>
</tr>
<tr>
<td>D05XI40</td>
<td>1544 ± 70</td>
<td>33 ± 0.4</td>
<td>76 ± 16</td>
</tr>
<tr>
<td>D10XI40</td>
<td>1580 ± 66</td>
<td>33 ± 1</td>
<td>75 ± 18</td>
</tr>
<tr>
<td>D30XI40</td>
<td>1597 ± 68</td>
<td>33 ± 0.3</td>
<td>118 ± 22</td>
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<tr>
<td>D60XI40</td>
<td>1731 ± 40</td>
<td>33 ± 0.3</td>
<td>48 ± 0</td>
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</table>

### Table A-6: Flexural properties of HDPE-D and HDPE-D/XI40 nanocomposites.

<table>
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<tr>
<th>Sample</th>
<th>Flexural modulus (MPa)</th>
<th>Flexural stress at yield (MPa)</th>
<th>Flexural strain at yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1270 ± 27</td>
<td>34 ± 0.2</td>
<td>7 ± 0.2</td>
</tr>
<tr>
<td>D02XI40</td>
<td>1281 ± 9</td>
<td>32 ± 0.5</td>
<td>7 ± 0.03</td>
</tr>
<tr>
<td>D05XI40</td>
<td>1280 ± 17</td>
<td>33 ± 0.4</td>
<td>8 ± 0.2</td>
</tr>
<tr>
<td>D10XI40</td>
<td>1284 ± 9</td>
<td>33 ± 0.2</td>
<td>7 ± 0.03</td>
</tr>
<tr>
<td>D30XI40</td>
<td>1362 ± 0</td>
<td>34 ± 0</td>
<td>7 ± 0</td>
</tr>
<tr>
<td>D60XI40</td>
<td>1611 ± 35</td>
<td>35 ± 0.6</td>
<td>7 ± 0.1</td>
</tr>
</tbody>
</table>
Table A-7: Tensile properties of HDPE-A and HDPE-A/YI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1180 ± 56</td>
<td>30 ± 1</td>
<td>291 ± 20</td>
</tr>
<tr>
<td>A02YI40</td>
<td>1235 ± 82</td>
<td>30 ± 1</td>
<td>274 ± 17</td>
</tr>
<tr>
<td>A05YI40</td>
<td>1251 ± 41</td>
<td>30 ± 1</td>
<td>270 ± 18</td>
</tr>
<tr>
<td>A10YI40</td>
<td>1297 ± 40</td>
<td>31 ± 0.3</td>
<td>275 ± 16</td>
</tr>
<tr>
<td>A30YI40</td>
<td>1455 ± 85</td>
<td>32 ± 0.1</td>
<td>311 ± 12</td>
</tr>
<tr>
<td>A60YI40</td>
<td>1698 ± 88</td>
<td>34 ± 1</td>
<td>336 ± 42</td>
</tr>
</tbody>
</table>

Table A-8: Flexural properties of HDPE-A and HDPE-A/YI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural modulus (MPa)</th>
<th>Flexural stress at yield (MPa)</th>
<th>Flexural strain at yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1095 ± 32</td>
<td>31 ± 0.4</td>
<td>7 ± 0.1</td>
</tr>
<tr>
<td>A02YI40</td>
<td>1130 ± 29</td>
<td>32 ± 0.2</td>
<td>8 ± 0.2</td>
</tr>
<tr>
<td>A05YI40</td>
<td>1157 ± 12</td>
<td>31 ± 0.03</td>
<td>8 ± 0.02</td>
</tr>
<tr>
<td>A10YI40</td>
<td>1181 ± 28</td>
<td>32 ± 0.4</td>
<td>8 ± 0.1</td>
</tr>
<tr>
<td>A30YI40</td>
<td>1367 ± 27</td>
<td>33 ± 0.4</td>
<td>7 ± 0.03</td>
</tr>
<tr>
<td>A60YI40</td>
<td>1610 ± 60</td>
<td>36 ± 0.3</td>
<td>7 ± 0.2</td>
</tr>
</tbody>
</table>
Table A-9: Tensile properties of HDPE-C and HDPE-C/Y140 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>597 ± 43</td>
<td>26 ± 1</td>
<td>204 ± 4</td>
</tr>
<tr>
<td>C02Y140</td>
<td>598 ± 52</td>
<td>25 ± 0.2</td>
<td>191 ± 2</td>
</tr>
<tr>
<td>C05Y140</td>
<td>617 ± 51</td>
<td>25 ± 0.2</td>
<td>189 ± 3</td>
</tr>
<tr>
<td>C10Y140</td>
<td>626 ± 51</td>
<td>25 ± 1</td>
<td>183 ± 14</td>
</tr>
<tr>
<td>C30Y140</td>
<td>716 ± 26</td>
<td>25 ± 0.2</td>
<td>187 ± 3</td>
</tr>
<tr>
<td>C60Y140</td>
<td>952 ± 44</td>
<td>26 ± 0.1</td>
<td>157 ± 31</td>
</tr>
</tbody>
</table>

Table A-10: Flexural properties of HDPE-A and HDPE-A/Y140 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural modulus (MPa)</th>
<th>Flexural stress at yield (MPa)</th>
<th>Flexural strain at yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>520 ± 10</td>
<td>19 ± 0.3</td>
<td>9 ± 0.3</td>
</tr>
<tr>
<td>C02Y140</td>
<td>527 ± 7</td>
<td>19 ± 0.2</td>
<td>8 ± 0.1</td>
</tr>
<tr>
<td>C05Y140</td>
<td>548 ± 6</td>
<td>19 ± 0.1</td>
<td>8 ± 0.2</td>
</tr>
<tr>
<td>C10Y140</td>
<td>587 ± 9</td>
<td>20 ± 0.1</td>
<td>8 ± 0.1</td>
</tr>
<tr>
<td>C30Y140</td>
<td>728 ± 6</td>
<td>22 ± 0.1</td>
<td>8± 0.14</td>
</tr>
<tr>
<td>C60Y140</td>
<td>996 ± 29</td>
<td>25 ± 0.03</td>
<td>8 ± 0.2</td>
</tr>
</tbody>
</table>
Table A-11: Tensile properties of HDPE-D and HDPE-D/YI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1338 ± 57</td>
<td>30 ± 0.2</td>
<td>77 ± 0.1</td>
</tr>
<tr>
<td>D02YI40</td>
<td>1374 ± 76</td>
<td>31 ± 1</td>
<td>105 ± 26</td>
</tr>
<tr>
<td>D05YI40</td>
<td>1372 ± 28</td>
<td>31 ± 1</td>
<td>121 ± 66</td>
</tr>
<tr>
<td>D10YI40</td>
<td>1387 ± 74</td>
<td>32 ± 1</td>
<td>162 ± 30</td>
</tr>
<tr>
<td>D30YI40</td>
<td>1481 ± 56</td>
<td>32 ± 0.2</td>
<td>264 ± 68</td>
</tr>
<tr>
<td>D60YI40</td>
<td>1755 ± 73</td>
<td>32 ± 1</td>
<td>95 ± 22</td>
</tr>
</tbody>
</table>

Table A-12: Flexural properties of HDPE-D and HDPE-D/YI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural modulus (MPa)</th>
<th>Flexural stress at yield (MPa)</th>
<th>Flexural strain at yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1270 ± 27</td>
<td>34 ± 0.2</td>
<td>7 ± 0.2</td>
</tr>
<tr>
<td>D02YI40</td>
<td>1318 ± 33</td>
<td>35 ± 0.1</td>
<td>7 ± 0.1</td>
</tr>
<tr>
<td>D05YI40</td>
<td>1352 ± 7</td>
<td>35 ± 0.1</td>
<td>7 ± 0.2</td>
</tr>
<tr>
<td>D10YI40</td>
<td>1426 ± 50</td>
<td>36 ± 0.6</td>
<td>8 ± 0.1</td>
</tr>
<tr>
<td>D30YI40</td>
<td>1485 ± 27</td>
<td>36 ± 0.3</td>
<td>7 ± 0.1</td>
</tr>
<tr>
<td>D60YI40</td>
<td>1629 ± 61</td>
<td>37 ± 0.5</td>
<td>7 ± 0.2</td>
</tr>
</tbody>
</table>
Table A-13: Tensile properties of HDPE-A and HDPE-A/ZI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1260 ± 16</td>
<td>28 ± 1</td>
<td>314 ± 15</td>
</tr>
<tr>
<td>A05ZI40</td>
<td>1302 ± 44</td>
<td>28 ± 0.4</td>
<td>311 ± 21</td>
</tr>
<tr>
<td>A10ZI40</td>
<td>1397 ± 35</td>
<td>28 ± 1</td>
<td>337 ± 16</td>
</tr>
<tr>
<td>A30ZI40</td>
<td>1561 ± 43</td>
<td>30 ± 0.2</td>
<td>291 ± 26</td>
</tr>
<tr>
<td>A60ZI40</td>
<td>1689 ± 47</td>
<td>31 ± 1</td>
<td>216 ± 25</td>
</tr>
</tbody>
</table>

Table A-14: Flexural properties of HDPE-A and HDPE-A/ZI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural modulus (MPa)</th>
<th>Flexural stress at yield (MPa)</th>
<th>Flexural strain at yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>923 ± 14</td>
<td>26 ± 0.1</td>
<td>8 ± 0.1</td>
</tr>
<tr>
<td>A05ZI40</td>
<td>985 ± 27</td>
<td>27 ± 0.1</td>
<td>8 ± 0.1</td>
</tr>
<tr>
<td>A10ZI40</td>
<td>1143 ± 36</td>
<td>29 ± 0.3</td>
<td>8 ± 0.2</td>
</tr>
<tr>
<td>A30ZI40</td>
<td>1487 ± 22</td>
<td>31 ± 0.2</td>
<td>7 ± 0.1</td>
</tr>
<tr>
<td>A60ZI40</td>
<td>1611 ± 35</td>
<td>35 ± 0.6</td>
<td>7 ± 0.1</td>
</tr>
</tbody>
</table>
Table A-15: Tensile properties of HDPE-C and HDPE-C/ZI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>561 ± 31</td>
<td>23 ± 0.5</td>
<td>180 ± 4</td>
</tr>
<tr>
<td>C05ZI40</td>
<td>604 ± 13</td>
<td>22 ± 0.3</td>
<td>163 ± 9</td>
</tr>
<tr>
<td>C10ZI40</td>
<td>643 ± 18</td>
<td>22 ± 0.3</td>
<td>147 ± 9</td>
</tr>
<tr>
<td>C30ZI40</td>
<td>754 ± 20</td>
<td>23 ± 0.4</td>
<td>117 ± 7</td>
</tr>
<tr>
<td>C60ZI40</td>
<td>1150 ± 38</td>
<td>26 ± 0.3</td>
<td>166 ± 15</td>
</tr>
</tbody>
</table>

Table A-16: Flexural properties of HDPE-A and HDPE-C/ZI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural modulus (MPa)</th>
<th>Flexural stress at yield (MPa)</th>
<th>Flexural strain at yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>434 ± 7</td>
<td>16 ± 0.1</td>
<td>9 ± 0.3</td>
</tr>
<tr>
<td>C05ZI40</td>
<td>458 ± 6</td>
<td>17 ± 0.1</td>
<td>9 ± 0.3</td>
</tr>
<tr>
<td>C10ZI40</td>
<td>487 ± 7</td>
<td>17 ± 0.1</td>
<td>9 ± 0.3</td>
</tr>
<tr>
<td>C30ZI40</td>
<td>611 ± 9</td>
<td>19 ± 0.2</td>
<td>8 ± 0.1</td>
</tr>
<tr>
<td>C60ZI40</td>
<td>816 ± 10</td>
<td>22 ± 0.1</td>
<td>11 ± 0.2</td>
</tr>
</tbody>
</table>
### Table A-17: Tensile properties of HDPE-D and HDPE-D/ZI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1441 ± 49</td>
<td>29 ± 0.4</td>
<td>127 ± 38</td>
</tr>
<tr>
<td>D05ZI40</td>
<td>1547 ± 38</td>
<td>29 ± 0.4</td>
<td>195 ± 40</td>
</tr>
<tr>
<td>D10ZI40</td>
<td>1563 ± 40</td>
<td>30 ± 0.1</td>
<td>258 ± 35</td>
</tr>
<tr>
<td>D30ZI40</td>
<td>1669 ± 15</td>
<td>30 ± 0.3</td>
<td>153 ± 39</td>
</tr>
<tr>
<td>D60ZI40</td>
<td>1846 ± 54</td>
<td>31 ± 0.3</td>
<td>46 ± 3</td>
</tr>
</tbody>
</table>

### Table A-18: Flexural properties of HDPE-D and HDPE-D/ZI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural modulus (MPa)</th>
<th>Flexural stress at yield (MPa)</th>
<th>Flexural strain at yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1201 ± 22</td>
<td>30 ± 0.2</td>
<td>7 ± 0.2</td>
</tr>
<tr>
<td>D05ZI40</td>
<td>1266 ± 12</td>
<td>31 ± 0.3</td>
<td>7 ± 0.3</td>
</tr>
<tr>
<td>D10ZI40</td>
<td>1290 ± 33</td>
<td>31 ± 0.3</td>
<td>7 ± 0.01</td>
</tr>
<tr>
<td>D30ZI40</td>
<td>1434 ± 9</td>
<td>32 ± 0.4</td>
<td>7 ± 0.2</td>
</tr>
<tr>
<td>D60ZI40</td>
<td>1509 ± 79</td>
<td>33 ± 0.2</td>
<td>7 ± 0.2</td>
</tr>
</tbody>
</table>
Appendix B

Mechanical Properties of HDPEs and HDPE/organoclay nanocomposites
(Single Step Process)

Table B-1: Tensile properties of HDPE-A and HDPE-A/YI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1239 ± 61</td>
<td>29 ± 1</td>
<td>285 ± 23</td>
</tr>
<tr>
<td>A02YI40</td>
<td>1260 ± 102</td>
<td>30 ± 2</td>
<td>316 ± 31</td>
</tr>
<tr>
<td>A05YI40</td>
<td>1299 ± 58</td>
<td>29 ± 1</td>
<td>318 ± 45</td>
</tr>
<tr>
<td>A10YI40</td>
<td>1304 ± 60</td>
<td>31 ± 1</td>
<td>334 ± 49</td>
</tr>
<tr>
<td>A30YI40</td>
<td>1396 ± 40</td>
<td>31 ± 1</td>
<td>276 ± 16</td>
</tr>
<tr>
<td>A60YI40</td>
<td>1521 ± 47</td>
<td>32 ± 1</td>
<td>211 ± 7</td>
</tr>
</tbody>
</table>

Table B-2: Flexural properties of HDPE-A and HDPE-A/YI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural modulus (MPa)</th>
<th>Flexural stress at yield (MPa)</th>
<th>Flexural strain at yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>959 ± 38</td>
<td>28 ± 0.3</td>
<td>8 ± 0.03</td>
</tr>
<tr>
<td>A02YI40</td>
<td>1047 ± 11</td>
<td>28 ± 0.2</td>
<td>8 ± 0.1</td>
</tr>
<tr>
<td>A05YI40</td>
<td>1074 ± 39</td>
<td>29 ± 0.1</td>
<td>8 ± 0.1</td>
</tr>
<tr>
<td>A10YI40</td>
<td>1082 ± 30</td>
<td>29 ± 0.2</td>
<td>8 ± 0.1</td>
</tr>
<tr>
<td>A30YI40</td>
<td>1215 ± 29</td>
<td>31 ± 0.2</td>
<td>8 ± 0.2</td>
</tr>
<tr>
<td>A60YI40</td>
<td>1513 ± 19</td>
<td>33 ± 0.3</td>
<td>8 ± 0.2</td>
</tr>
</tbody>
</table>
Table B-3: Tensile properties of HDPE-A and HDPE-A/ZI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1260 ± 16</td>
<td>28 ± 0.5</td>
<td>314 ± 15</td>
</tr>
<tr>
<td>A05ZI40</td>
<td>1310 ± 18</td>
<td>28 ± 0.7</td>
<td>313 ± 13</td>
</tr>
<tr>
<td>A10ZI40</td>
<td>1350 ± 58</td>
<td>28 ± 0.4</td>
<td>303 ± 45</td>
</tr>
<tr>
<td>A30ZI40</td>
<td>1508 ± 38</td>
<td>29 ± 0.4</td>
<td>200 ± 19</td>
</tr>
<tr>
<td>A60ZI40</td>
<td>1680 ± 37</td>
<td>30 ± 0.2</td>
<td>171 ± 32</td>
</tr>
</tbody>
</table>

Table B-4: Flexural properties of HDPE-A and HDPE-A/ZI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural modulus (MPa)</th>
<th>Flexural stress at yield (MPa)</th>
<th>Flexural strain at yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>923 ± 14</td>
<td>26 ± 0.1</td>
<td>8 ± 0.1</td>
</tr>
<tr>
<td>A05ZI40</td>
<td>936 ± 32</td>
<td>26 ± 0.3</td>
<td>8 ± 0.1</td>
</tr>
<tr>
<td>A10ZI40</td>
<td>956 ± 29</td>
<td>27 ± 0.2</td>
<td>8 ± 0.1</td>
</tr>
<tr>
<td>A30ZI40</td>
<td>1137 ± 41</td>
<td>28 ± 0.2</td>
<td>8 ± 0.1</td>
</tr>
<tr>
<td>A60ZI40</td>
<td>1418 ± 63</td>
<td>30 ± 0.3</td>
<td>8 ± 0.1</td>
</tr>
</tbody>
</table>
Table B-5: Tensile properties of HDPE-C and HDPE-C/ZI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>561 ± 31</td>
<td>23 ± 1</td>
<td>180 ± 4</td>
</tr>
<tr>
<td>C05ZI40</td>
<td>611 ± 9</td>
<td>21 ± 1</td>
<td>147 ± 16</td>
</tr>
<tr>
<td>C10ZI40</td>
<td>629 ± 23</td>
<td>21 ± 0.1</td>
<td>157 ± 38</td>
</tr>
<tr>
<td>C30ZI40</td>
<td>856 ± 17</td>
<td>24 ± 1</td>
<td>437 ± 19</td>
</tr>
<tr>
<td>C60ZI40</td>
<td>1142 ± 48</td>
<td>25 ± 0.4</td>
<td>350 ± 28</td>
</tr>
</tbody>
</table>

Table B-6: Flexural properties of HDPE-C and HDPE-C/ZI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural modulus (MPa)</th>
<th>Flexural stress at yield (MPa)</th>
<th>Flexural strain at yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>434 ± 7</td>
<td>16 ± 0.1</td>
<td>9 ± 0.3</td>
</tr>
<tr>
<td>C05ZI40</td>
<td>460 ± 5</td>
<td>17 ± 0.2</td>
<td>9 ± 0.3</td>
</tr>
<tr>
<td>C10ZI40</td>
<td>499 ± 4</td>
<td>17 ± 0.1</td>
<td>9 ± 0.2</td>
</tr>
<tr>
<td>C30ZI40</td>
<td>628 ± 15</td>
<td>19 ± 0.3</td>
<td>8 ± 0.1</td>
</tr>
<tr>
<td>C60ZI40</td>
<td>846 ± 5</td>
<td>22 ± 0.1</td>
<td>8 ± 0.1</td>
</tr>
</tbody>
</table>
Table B-7: Tensile properties of HDPE-D and HDPE-D/ZI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1441 ± 49</td>
<td>29 ± 0.4</td>
<td>127 ± 38</td>
</tr>
<tr>
<td>D05ZI40</td>
<td>1539 ± 37</td>
<td>29 ± 0.2</td>
<td>232 ± 20</td>
</tr>
<tr>
<td>D10ZI40</td>
<td>1613 ± 32</td>
<td>30 ± 0.3</td>
<td>220 ± 23</td>
</tr>
<tr>
<td>D30ZI40</td>
<td>1662 ± 41</td>
<td>30 ± 0.4</td>
<td>102 ± 31</td>
</tr>
<tr>
<td>D60ZI40</td>
<td>1837 ± 41</td>
<td>31 ± 0.5</td>
<td>42 ± 6</td>
</tr>
</tbody>
</table>

Table B-8: Flexural properties of HDPE-D and HDPE-D/ZI40 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural modulus (MPa)</th>
<th>Flexural stress at yield (MPa)</th>
<th>Flexural strain at yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1201 ± 22</td>
<td>30 ± 0.2</td>
<td>7 ± 0.3</td>
</tr>
<tr>
<td>D05ZI40</td>
<td>1278 ± 4</td>
<td>31 ± 0.3</td>
<td>7 ± 0.1</td>
</tr>
<tr>
<td>D10ZI40</td>
<td>1277 ± 16</td>
<td>31 ± 0.1</td>
<td>7 ± 0.2</td>
</tr>
<tr>
<td>D30ZI40</td>
<td>1378 ± 55</td>
<td>32 ± 0.1</td>
<td>7 ± 0.1</td>
</tr>
<tr>
<td>D60ZI40</td>
<td>1560 ± 97</td>
<td>32 ± 0.4</td>
<td>7 ± 0.1</td>
</tr>
</tbody>
</table>
VITA

Ponusa Songtipya

Ponusa Songtipya was born in August 18, 1976 in Bangkok, Thailand. In 1998, she received a B.Sc. with honors in Chemistry from Prince of Songkla University, Songkla, Thailand. In 2002, she received a M.Sc. in Polymer Science and Technology from Mahidol University, Bangkok, Thailand.

In 2004, she entered Graduate Program at The Pennsylvania State University to pursue her Ph.D. in Materials Science and Engineering.