POLYOLEFIN-CLAY NANOCOMPOSITES PREPARED WITH AID OF POWER ULTRASOUND

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ABSTRACT

A continuous ultrasound assisted process using a single screw extruder with an ultrasonic attachment was developed to prepare polyolefin/clay nanocomposites of varying clay concentrations. Isotactic polypropylene (PP) and high density polyethylene (HDPE) were chosen as a polymeric matrix. A partial intercalation of polymer molecules into clay galleries, which occurs at short residence times (on the order of seconds), was observed, as evident from the measurements by X-ray diffraction and transmission electron microscopy. The obtained results indicated the rapid intercalation of polyolefin/clay nanocomposite without the matrix being chemically modified.

Two methods for fabrication of PP/clay nanocomposites using a continuous ultrasound assisted process were compared. In the first approach, where a two stage process was implemented, the nanocomposites were prepared using a co-rotating twin screw extruder followed by a single screw extruder equipped with ultrasonic die attachment. In the second method, where a single stage process was used, the nanocomposites were compounded by a single screw extruder with two mixing sections and ultrasonic die attachment. Single stage process led to less polymer degradation at the fixed gap size. Variations of flood and starved feeding, and gap size during single stage process were studied. Results indicate that intercalation and matrix degradation under ultrasound were higher for flood feeding and for smaller gap. Both single and two stage
processes produced PP based nanocomposites exhibiting higher elongation at break and toughness.

The melt intercalation of HDPE/clay nanocomposites was also observed under ultrasonic treatment at various amplitudes leading to increase of the elongation at break and toughness. The Young’s modulus of untreated and treated nanocomposites increased significantly with the increase of clay loading. But the modulus of treated samples showed lower values than that of untreated ones. Oxygen permeability of treated HDPE/clay nanocomposites was reduced up to 20% as compared to untreated samples.

The effect of ultrasound on the structure and properties of nanocomposites prepared from PP/maleated PP/clay blends was evaluated. No synergetic effect between polypropylene modified with maleic anhydride and treatment by high power ultrasound in preparation of nanocomposites has been detected.

The modified Halpin-Tsai theory of composite materials has been employed in order to predict the effect of incomplete exfoliation of clay platelets on the Young’s modulus of the nanocomposites. A good agreement between experimental and theoretical data has been observed when reduction of the reinforcement efficiency of clay had been incorporated through reduced aspect ratio of elementary clay platelets.
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DEDICATION

To my mother Olga, father Valery, and brother Andrei
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CHAPTER I
INTRODUCTION

The studies on nanocomposites began in the early 1980s at Toyota Central Research Laboratories\(^1\). The first licensee of Toyota’s nanocomposite technology was Ube Industries, which developed a polyamide clay nanocomposite\(^2\). Since then the field of polymer nanocomposites has attracted considerable attention as a method of enhancing polymer properties and extending their utility, by using molecular or nanoscale reinforcement rather than conventional particulate filled microcomposites goods\(^3,4\).

Nanocomposites are a combination of two or more phases containing different compositions or structures, where at least one the phases is in the nanoscale regime. These materials exhibit behavior different from conventional composite with microscale structure, due to the small size of the structural unit and the high aspect ratio\(^5\). The properties of composite materials are greatly influenced by the degree of mixing between the two phases. In conventionally filled polymers, the constituents are immiscible, resulting in a coarsely blended macrocomposite with chemically distinct phases. It results in poor physical attraction between the organic and inorganic components, leading to agglomeration of the latter, and therefore, weaker materials. In addition, the micrometer size particles act as stress concentrators. In nanocomposites, chemically dissimilar
components are combined at the nanometer scale and are too small to be stress concentrators. Stronger interaction between the polymer and filler produces materials with improved properties. Examples of improvements are the increase in strength, modulus, thermal resistance, heat distortion temperature, and solvent resistance, and reductions in flammability and gas permeation at very low loading (2-5 wt %). All of the above can be reached only if the clay layered structure is separated (exfoliated), and then well dispersed into the polymeric matrix.

Since work in this area has been accelerating at a considerable pace, it is worth mentioning different types of polymers being improved by the introduction of the clay and clay-like platelets. These polymers include poly(ethyleneterephthalate), poly(ε-caprolactone), and unsaturated polyesters, polyurethanes, polystyrene, polypropylene, polyethylene, poly(methyl methacrylate), poly(ethylene oxide), polyimides, liquid-crystalline polymers, epoxy polymers, and phenolic resins.

Let us focus on polypropylene, which is one of the fastest growing classes of thermoplastics. This growth is attributed to its attractive combination of low cost, low density, and high heat distortion temperature. The extraordinary versatility of unfilled virgin resin and reinforced polypropylene suits a wide spectrum of end-use applications for fiber, films, and molded parts. However, there always exist certain shortcomings in physical and chemical properties that can limit universal use of any given polymer resin. In packaging, for example, polypropylene resins have poor oxygen barriers, while low dimensional and thermal stability limits the scope of polypropylene composites in
automotive applications\textsuperscript{61}. One of the schemes to improve the above properties involves filling of polypropylene matrix with organically modified montmorillonite. Although the main challenge in preparation of such composites is that polypropylene being too much apolar to correctly interact with the modified layers\textsuperscript{62}.

When nanocomposites are formed, they exhibit significant improvements in physical, chemical, and mechanical properties. Usually at very low loading, nanocomposites show a greatly improved tensile strength, stiffness, better dimensional stability, decreased thermal expansion coefficient, and reduced gas permeation properties in comparison with neat or unfilled polymer resin. In both academic and industrial enterprises, the study of polypropylene nanocomposites is an intense area of current interest and investigation. The driving force for such efforts is attributed to huge commercial opportunities in both automotive and packaging applications. Material design at relatively low clay loading addresses the inherent shortcomings of polypropylene resin by itself and does so with favorable cost, processing, and reduced molded-part weight profiles\textsuperscript{61}.

An example of successful implementation of polypropylene nanocomposites is GM, which used the material for a step assist on the 2002 Chevrolet Astro and GMC Safari vans. The program represents the first commercial application of a TPO with nanoscale filler, one that automaker and its development partners predict will be used extensively in future programs once the material proves itself on the van\textsuperscript{63}. In a Principia Partners study published before the GM announcement, analysts predicted automaker
could use about 20 million pounds of polyolefin nanocomposites by 2005, with substantial
growth to follow, perhaps growing to 200 million pounds by 2010⁶⁴.

Huge potential for polymer nanostructured materials exists across the military
scene, from aerospace to the U.S. Army foot soldier. The US Air Force is examining
polymer-layered silicate nanocomposites for next-generation polymeric composites for use
in unmanned aerial vehicles. Other investigators look at the material’s use in anti-
flammability additives for aircraft interiors, gas-vapor barriers for food packaging industry
and barrier liners for cryogenic fuels in aerospace systems. Some experiments are done
aboard the International Space Station⁶⁵.

Emerging technologies involving nanomaterials and nanocomposites surfaced
through a panel discussion of top government scientists and the presentation of 22 mostly
academic technical papers. Ten federal agencies spent $694 million on nanotechnology
research and development during the fiscal year ended Sept. 30, 2003. Funding of $774
million is projected in the current fiscal year as the NSF specified⁶⁶.

In spite of relatively good funding and the large number of researchers working
on preparation of polypropylene-clay nanocomposites no direct intercalation of polymer in
simply organically modified layered silicates has been observed due to polymeric matrix
apolarity. Two different techniques were used to overcome this problem. The first one is
functionalization of the polypropylene chain by either maleic anhydride or hydroxyl
groups⁶⁷. In the second technique a commercially available organoammonium-exchanged
montmorillonite was modified using an organic swelling agent (whose boiling point is
situated between 100 and 200°C, such as ethylene glycol, naphtha or heptane) in order to
increase the interlayer spacing. The swollen organo-clay was then compounded with polypropylene in a twin-screw extruder at 250°C. The swelling agent was volatilized during extrusion process, leading to the formation of a ‘nano’ composite. As one can see, both methods use additional chemicals and what is more the second way is not an environment friendly.

Over the past several decades, a number of studies of the effects of ultrasound on polymers have been performed and reported. It was observed that long-chain polymer molecules can be ruptured by high intensity ultrasound during melt extrusion. The breakage of the C-C bond by ultrasound usually leads to the formation of long-chain radicals. In polymer-filler systems, polymeric radicals may terminate on the clay surface or combine with the surface modifying agent (in the case of organo-clay) forming a chemical bond.

Several studies about application of ultrasound in nanocomposite preparation were published within last three years. One of them was on preparation and characterization of nickel-polystyrene nanocomposite, the second one was on preparation of conductive polyaniline-nanosilica particle composites, the third one described silica agglomerate breakdown in continuous ultrasonic extruder. They all claim that ultrasound may assist in better filler dispersion. Finally, an attempt to develop polypropylene-clay nanocomposite via melt intercalation in intensive batch mixer equipped with powerful ultrasound was reported.

The main objectives of this study are:
1) Development of continuous process for preparation of polyolefin-clay composites using high power ultrasound under different processing conditions.

2) Identification of the processing conditions for possible intercalation/exfoliation.

3) Investigation of the polymeric matrix type effect on properties of obtained materials.

4) To study the effects of ultrasound wave on properties of polyolefin/clay nanocomposites.

5) To consider the effect of maleic anhydride as a compatibilizer.
CHAPTER II
LITERATURE SURVEY AND BACKGROUND

2.1 Montmorillonite (MMT) Clays

Natural clays are most commonly formed by the in situ alteration of volcanic ash. Another less common origin is the hydrothermal alteration of volcanic rocks. The focus of this discussion is the former. Montmorillonite originates from volcanic eruptions during the Cretaceous period (85 – 125 million years ago).

Molten rock within the planet, magma, under extreme pressure, forced its way through the earth’s crust and exploded into the atmosphere in a volcanic eruption. The rain of airborne ash carried on the prevailing winds from the eruption clouds subsequently fell to earth forming deposits characterized by high volume bedding of well-to-moderately sorted ash. The parent ash was deposited under marine conditions, as well as some minor accumulation in alkaline lakes.

Opinions differ concerning the process and time of alteration of the ash to clay. Certainly the change began with contact with water. The instability of the ash made for ease of dissolution and reaction with the available marine chemistry. Probably the most important single factor in the formation of the clay was the availability of sufficient
magnesium in the marine sediment environment\textsuperscript{76}. The layered silicates commonly used in nanocomposites belong to the structural family known as 2:1 phylosilicates.

2.1.1 Structure

Silica is the dominant constituent of clays, with alumina being essential, as well. Clays have a sheet structure consisting of 2 types of layers, the silica tetrahedral and Al\textsuperscript{3+} octahedral layers. The silica tetrahedral layer consists of SiO\textsubscript{4} groups linked together to form a hexagonal network of the repeating units of composition Si\textsubscript{4}O\textsubscript{10}. The two tetrahedral layers sandwich the octahedral, sharing their apex oxygens with the latter. These three layers form one clay sheet. The inner Al(Mg, Fe)O\textsubscript{4}(OH)\textsubscript{4} layer consists of two sheets of close packed oxygen atoms or hydroxyls between which octahedrally coordinated aluminum atoms are imbedded in such a position that they are equidistant from six oxygen atoms or hydroxyl groups. Some of the Al\textsuperscript{3+} are substituted by Mg\textsuperscript{2+} or Fe\textsuperscript{2+} causing a net negative charge on the platelet. The electrical imbalance is corrected by the presence of counter cations, like Na\textsuperscript{+}. It let use quaternary ammonium cations to ion exchange with Na\textsuperscript{+}, which allows making the inorganic MMT platelet surface organic\textsuperscript{77}. 
2.1.2 Properties

Chemical formula of commonly used montmorillonite is \( M_x(Al_{4-x}Mg_2)Si_8O_{20}(OH)_4 \), where \( M \) is the monovalent cation like Li, Na, Rb, Cs, \( x \) is the degree of isomorphous substitution (between 0.5 and 1.3)\(^62\).

The crystalline structure of MMT was characterized by Hofmann et al\(^78\). The elementary unit cell is \( a=5.20 \, \text{Å}, \, b=8.56 \, \text{Å}, \, c=9.5 \, \text{Å} \), where the \( c \) represents the elementary layer thickness. The lateral dimensions of these layers may vary from 200 to 2000 nm, so an aspect ratio of 1000 can be realized upon complete exfoliation of nanolayers from tactoids that are typically 0.1-1 \( \mu \)m thick\(^79\).

As the forces that hold the stacks together are relatively weak, the intercalation of small molecules between the layers is easy\(^80\). In order to render these hydrophilic phyllosilicates more organophilic, the hydrated cations of the interlayer can be exchanged with cationic surfactants such as alkylammonium or alkylphosphonium (onium). The modified clay (or organoclay) being organophilic, its surface energy is lowered and is more compatible with organic polymers. These polymers may be able to intercalate within the galleries to form a nanocomposite\(^62\).

Montmorillonite is characterized by a moderate negative surface charge (known as the cation exchange capacity (CEC) and expressed in meq/100g). The charge of the layer is not locally constant as it varies from layer to layer and must rather be considered as an average value over the whole crystal. Proportionally, even if a small part of the charge balancing cations is located on the external crystallite surface, the majority of these exchangeable cations are located inside the galleries. When the hydrated cations are
ion-exchanged with organic cations such as more bulky alkylammoniums, it usually results in a larger interlayer spacing\textsuperscript{62}.

2.1.3 Organoclays

The occurrence of cation exchange reaction between montmorillonite and ammonium compounds was found by Smith\textsuperscript{81,82}. To prepare organophilic montmorillonite, Jordan used aliphatic ammonium salts\textsuperscript{93}. Weiss intercalated montmorillonite with n-alkylammonium ions\textsuperscript{84}. The gallery spacing of the intercalated clay depends on the length of the alkyl chain.

Organoclays have been used for many applications such as absorbents, rheological additives for organic solvent, clay column chromatography, antioxidants for rubber materials, lubricants, and gel formation agents\textsuperscript{85-87}.

There are several organoclay manufacturers around the world such as Southern Clay Products (USA), Nanocor (USA), Elementis Specialties (USA), Akzo Chemicals (Netherlands), Fenghong Clay Chemicals Inc. (China). Among them Southern Clay Products (TX, USA) produces a broad variety of organoclays for different application areas, for example, personal care, pharmaceutical, paints and coatings, auto care, and oil drilling fluids. Cloisite\textsuperscript{TM} montmorillonite organoclays have been widely used by researchers to compound with polymers in attempts to make a nanocomposite because the exact chemical structure of organic modifiers is well known.
2.1.4 Advantages over conventional fillers

Montmorillonite can be employed in the preparation of polymer-clay nanocomposites. Typical performance advantages of montmorillonite compared to traditional reinforcing agents for plastics are as follows:

1. Montmorillonite will develop similar increase in modulus and tensile strength at 3-5% loading compared to 20-60% loading of conventional reinforcing agents such as kaolin, silica, talc, and carbon black. Implicit advantages include lighter plastic parts with greater transparency.

2. With montmorillonite, the plastic will have increased barrier properties to moisture, solvents, chemical vapors, gases such as O₂ and flavors. Particle shape is known to affect plastic barrier properties. Montmorillonite is a nanoparticle with an anisotropic, plate-like, high aspect-ratio morphology. It is this morphology that leads to the improved permeation barrier through a tortuous path mechanism.

3. With montmorillonite, the plastic will have increased dimensional stability at low reinforcement loading. Dramatic decreases in coefficient of linear thermal expansion values have been reported.

4. The plastic will have a higher heat distortion temperature. Only a few percent loading of montmorillonite will increase the temperature at which the plastic will begin to soften. This property is critical, for example, in under-the-hood automotive applications.

5. The thermoplastic polymer will be more recyclable. Montmorillonite performance actually improves upon recycling. Fiberglass products typically cannot be recycled for the
same application, since the fibers are damaged during the recycling process.
6. The plastic will dye easier. Due to the colloidal nature, high surface area, and surface
  treatability of montmorillonite, it can serve as an active site to fix dyes into plastic.
7. Nanocomposites offer a new flame-retardant approach. The improved flame retardancy
  as measured by Cone Calorimetry shows a decrease in the Peak Heat Release Rate. A
decrease in smoke and an increase in char formation are observed. NIST has formed a
consortium to study the flammability of polymer-clay nanocomposites.
8. The appearance of painted parts is improved compared to conventional reinforced
  parts. The nanocomposite particles are much smaller than traditional reinforcing agents so
the plastic surface is much smoother.
9. There is reduced static cling in films containing nanocomposites. This property was
observed in some work being done by Southern Clay Products personnel98.

2.2 Polymer-clay Nanocomposites

Depending on the nature of the components used (layered silicate, organic
cation and polymer matrix) and the method of preparation, three main types of
composites may be obtained when a layered clay is associated with a polymer. When the
polymer is unable to intercalate between the silicate sheets, a phase separated composite
is obtained, whose properties stay in the same range as traditional microcomposites.
Beyond this classical family of composites, two types of nanocomposites can be
recovered. Intercalated structure in which a single (and sometimes more than one)
extended polymer chain is intercalated between the silicate layers resulting in a well
ordered multilayer morphology built up with alternating polymeric and inorganic layers. When the silicate layers are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure is obtained.

2.2.1 Methods of preparation

Several strategies have been considered to prepare polymer-layered silicate nanocomposites. They include four main processes\(^9\):

2.2.1.1 Exfoliation-adsorption

The layered silicate is exfoliated into single layers using a solvent in which the polymer (or a prepolymer in case of insoluble polymers such as polyimide) is soluble. It is well known that such layered silicates, owing to the weak forces that stack the layers together can be easily dispersed in an adequate solvent. The polymer then adsorbs onto the delaminated sheets and when the solvent is evaporated (or the mixture precipitated), the sheets reassemble, sandwiching the polymer to form, in the best case, an ordered multilayer structure. The nanocomposites obtained through emulsion polymerization, where the layered silicate is dispersed in the aqueous phase, are also considered to derive through this process.

2.2.1.2 In situ intercalative polymerization

In this technique, the layered silicate is swollen within the liquid monomer (or a monomer solution) so as the polymer formation can occur in between the intercalated
sheets. Polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator or by an organic initiator or catalyst fixed through cationic exchange inside the interlayer before the swelling step by the monomer.

2.2.1.3 Melt intercalation

The layered silicate is mixed with the polymer matrix in the molten state. Under these conditions and if the layer surfaces are sufficiently compatible with the chosen polymer, the polymer can crawl into the interlayer space and form either an intercalated or an exfoliated nanocomposite. In this technique, no solvent is required.

2.2.1.4 Template synthesis

This technique, where the silicates are formed in situ in an aqueous solution containing the polymer and the silicate building blocks has been widely used for the synthesis of double-layer hydroxide-based nanocomposites\textsuperscript{90,91} but is far less developed for layered silicates. In this technique, based on self-assembly forces, the polymer aids the nucleation and growth of the inorganic host crystals and gets trapped within the layers as they grow.

2.2.2 Structure characterization

Several complementary techniques are used in order to differentiate between conventional microcomposite, intercalated, and exfoliated nanocomposites. The se are X-ray diffraction, transmission electron microscopy, and atomic force microscopy.
2.2.2.1 X-ray Diffraction (XRD)\textsuperscript{92}

XRD is used to identify intercalated structures. In such nanocomposites, the repetitive multilayer structure is well preserved, allowing the interlayer spacing to be determined. The intercalation of the polymer chains usually increases the interlayer spacing, in comparison with the spacing of the organoclay used, leading to a shift of the diffraction peak towards lower angle values (angle and layer spacing values being related through the Bragg's relation: $\lambda = 2dsin\theta$, where $\lambda$ corresponds to the wave length of the X-ray radiation used in the diffraction experiment, $d$ is the spacing between diffractional lattice planes and $\theta$ is the measured diffraction angle or glancing angle).

As far as exfoliated structure is concerned, no more diffraction peaks are visible in the XRD diffractograms either because of a much too large spacing between the layers (i.e. exceeding 8 nm in the case of ordered exfoliated structure) or because the nanocomposite does not present ordering anymore.

2.2.2.2 Transmission Electron Microscopy (TEM)\textsuperscript{93,94}

TEM is used to characterize the nanocomposite morphology. This technique allows observing visually an intercalated and an exfoliated nanocomposite. Besides these two well defined structures, other intermediate organizations can exist presenting both intercalation and exfoliation. In this case, a broadening of the diffraction peak is often observed and one must rely on TEM observation to define the overall structure.
2.2.2.3 Atomic Force Microscopy (AFM)

AFM is another powerful technique used to visualize nanocomposite structure. The resolution of AFM is principally atomic order and this guarantees a very high accuracy of AFM metrology. Furthermore, AFM can image three-dimensional shapes and does not require any coating or surface etching of the sample. The first atomic force microscopes operated in the contact mode. In that mode the tip, mounted onto the end of a flexible cantilever, raster scans the surface of the sample. The deflection of the cantilever due to tip-surface interaction, detected by a laser beam, reveals the sample surface. Small samples like nanoparticles are difficult to scan using contact mode because they are weakly immobilized to the surface and can be easily scraped off.

The specimen to be tested is placed on a piezoelectric tube scanner that enables an accurate scan in the horizontal (x-y) plane while moving in the vertical (z) direction.

Tapping mode atomic force microscopy (TM-AFM), first introduced in 1993, measures topography by tapping the surface with an oscillating probe tip so that the tip makes contact with the sample for only a short duration in each oscillation cycle. The method of operation results in lower lateral forces compared with conventional contact mode, so the irreversible destruction on soft surfaces can be eliminated. This method has been proven to give high quality images of softer substrates.

The whole tip-cantilever system is oscillated as it scans over the surface. As the tip is moved across the surface the interaction between the tip and the surface causes a change in the amplitude of the oscillations. In the experimental setup a topographic image is generated by measuring the height change of the tip needed to maintain constant
amplitude as a function of its position over the surface. Contrast in images is normally calibrated so that bright areas represent bigger tip-surface separation and dark areas represent smaller separation.

The cantilever, primarily made of silicon, is oscillated at a frequency $f_0$ of about 200-300 kHz and amplitude $A_L$, typically greater than 20 nm. When the sample surface is brought close to the tip, the magnitude of oscillation is considerably reduced, which generates a topographic signal; by monitoring these changes, an image representing surface topography can be obtained. The tip is moved very slowly across the surface at a scan speed about 2 Hz (four lines per second) and each pixel in the image is an average from several hundred oscillations. The fact that the tip is allowed to touch the surface provides a very high lateral resolution of 1-2 nm and a vertical resolution of 0.1 nm$^{99}$.

2.2.3 Nanocomposites’ properties

Layered silicate nanofillers have proved to trigger a tremendous properties improvement of the polymers in which they are dispersed. Amongst those properties, unexpected large increase in moduli (tensile or Young's modulus and flexural modulus) of nanocomposites at filler contents sometimes as low as 1 wt.% has drawn a lot of attention. Thermal stability and fire retardancy through char formation are other interesting and widely searched properties displayed by nanocomposites. Those new materials have also been studied and applied for their superior barrier properties against gas and vapor transmission$^{62}$.  

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2.2.3.1 Mechanical properties

The Young's modulus (or tensile modulus), expressing the stiffness of a material at the start of a tensile test, has shown to be strongly improved when nanocomposites are formed. Polypropylene (PP) nanocomposites obtained by melt intercalation have shown significant increase in the Young's modulus at rather low filler content. The amount of maleic anhydride-modified PP (PP-MA) added to increase intercalation (and to possibly favor exfoliation) is varied\textsuperscript{25}.

It has been observed that increasing the amount of PP-MA not only improves intercalation or partial exfoliation, but increases also the modulus value. Comparison of PP with the simple PP-MA/PP blends rules out any possible effect of some matrix modification due to the presence of increasing amounts of PP-MA.

In thermoplastic-based (intercalated or exfoliated) nanocomposites, the stress at break, which expresses the ultimate strength that the material can bear before break, may vary strongly depending on the nature of the interactions between the matrix and the filler.

As far as polypropylene-based nanocomposites are concerned\textsuperscript{25}, no or only very slight tensile stress enhancements are measured. This behavior can be partially explained by the lack of interfacial adhesion between apolar PP and polar layered silicates. Addition of maleic anhydride modified polypropylene to the polypropylene matrix has, however, proved to be favorable to the intercalation of the PP chains and maintains the ultimate stress at an acceptable level.

The effect of nanocomposite formation on the elongation at break has not been widely investigated. When dispersed in such thermoplastics as intercalated-exfoliated PP,
the elongation at break is reduced. This decrease is very important, dropping from 150 and 105% for a pure PP matrix and a 6.9 wt.% non-intercalated clay microcomposite, respectively, down to 7.5% for a PP-based nanocomposite filled with 5 wt.% silicate layers.

Dynamic mechanical analysis (DMA) measures the response of a given material to a cyclic deformation (usually tension or three-point bending type deformation) as a function of the temperature. DMA results are expressed by three main parameters: (i) the storage modulus (E'), corresponding to the elastic response to the deformation; (ii) the loss modulus (E''), corresponding to the plastic response to the deformation and (iii) tan δ, that is the (E''/E') ratio, useful for determining the occurrence of molecular mobility transitions such as the glass transition temperature.

An increase in the storage modulus is related to better nanoclay dispersion in the case of polypropylene-based nanocomposites. The degree of nanofiller dispersion can be tuned up either by using different amounts of a given PP modified with maleic anhydride (acid value=52 mg KOH/g) or can even be drawn towards the formation of exfoliated nanocomposites by playing with the relative functionalization content all along of the modified PP (using a PP-MA with an acid value=26 mg KOH/g). Varying the relative amount of PP-MA within the PP matrix highly modifies the temperature dependence of the storage modulus reducing its value of unfilled PP matrix. Below Tg (located around 13 °C for all the composites) the relative modulus values of the nanocomposites are not so much enhanced compared to the pure matrix while above Tg, an important increase of the moduli is observed, reaching a maximal value of 1.76 around 80 °C, in the case of the
PP-clay hybrid composite. On the other hand, the relative storage modulus of the PP-clay conventional microcomposite stays relatively low and quickly reaches a plateau value around 1.26. One can further observe that the storage moduli show a sharp decline above 140 °C. The main reason for this decline resides in the fact that the softening point of the PP-MA matrix is reached at this temperature, strongly reducing the elastic response of the material.

A two-fold increase in the relative moduli \((E'/E'_{\text{matrix}})\) is achieved for a nanocomposite based on organo-modified montmorillonite nanoparticles. Interestingly enough, a maximum value of 2.4 is reached by substituting synthetic fluorinated mica with montmorillonite. The difference in behavior of the two types of filler was not explained by the authors, but it is more likely related to the respective aspect ratio of the dispersed particles, since mica layers are known to be much longer than montmorillonite layers.

In summary, the storage modulus appears to be substantially enhanced at temperatures above \(T_g\) for exfoliated nanocomposites filled with layered silicates of high aspect ratio. A possible explanation for such an improvement could be the creation of a three-dimensional network of interconnected long silicate layers, strengthening the material through mechanical percolation\(^{62}\).

2.2.3.2 Gas permeability

The high aspect ratio characteristic of silicate nanolayers in exfoliated nanocomposites has been found to highly reduce the gas permeability in films prepared
from such nanomaterials. The impermeable clay layers mandate a tortuous pathway for a permeant to pass through the nanocomposites. The enhanced barrier characteristics, chemical resistance, reduced solvent uptake and flame retardance of clay-polymer nanocomposites all benefit from the hindered diffusion pathways through the nanocomposites\(^ {101}\). The tortuous path theory has been well accepted for filled polymer systems\(^ {102}\). According to this theory, the impermeable inorganic filler in the relatively permeable polymer matrix will create a “tortuous path” for the diffusing molecules.

As a result, the filled polymer demonstrates reduced gas permeability. The permeability can be determined using the following equation:

\[
P_f/P_u = \phi_p/[1 + (L/2W)\phi_f],
\]

where \(P_f\) and \(P_u\) are the permeability of the filled and unfilled polymer, \(\phi_p\) and \(\phi_f\) are the volume fraction of the polymer and filler, and \(L/W\) is the aspect ratio of the filler. According to this theory, there is an inverse relationship between aspect ratio of the filler and permeability of the filled polymer. An increase in aspect ratio of the filler corresponds to decrease in the permeability of the filled polymer.

Compared with most inorganic fillers, silicate layers of montmorillonite have very high aspect ratio. The thickness of the single layer is 1 nm, while the length is in the range 200-2,000 nm. When the layered silicate is fully exfoliated in the polymer matrix, greatly reduced gas permeability can be achieved. So in order to reduce the gas permeability of polypropylene nanocomposites, it is important to fully disperse the silicate layers into polypropylene matrix. Sometimes, if the dispersion of the silicate is
not good, there is almost no improvement in permeability; even increased permeability has been observed in some extreme cases.

2.2.3.3 Thermal and dimensional stability

The thermal stability of a material is usually assessed by thermogravimetric analysis (TGA) where the sample mass loss due to volatilization of degraded by-products is monitored in function of a temperature ramp. When the heating is operated under an inert gas flow (nitrogen, helium), a non-oxidative degradation occurs while the use of air or oxygen allows to follow the oxidative degradation of the sample.

The incorporation of clay in a platelet form is known to result in the improvement of the thermal stability of polymers\(^4\), 14, 103-106. Such, the thermal degradation of pure PP and its nanocomposites containing 1, 2, and 4 wt % of MMT at a heating rate of 40°C/min happens at 479, 540, 536, and 530 °C accordingly\(^106\).

Heat Distortion Temperature (HDT) is another important characteristic of composites used to estimate its dimensional stability at elevated temperature. The HDT can be determined from the storage modulus versus temperature curves of the dynamic mechanical analysis. According to ASTM D-648, HDT is defined as the temperature when flexural modulus of the sample is 145 MPa. The HDT values of the PP/clay nanocomposites are changing from 110 °C for pure PP to 151 °C for its 8.1 wt% nanocomposite\(^105\).

An additional benefit from the addition of layered silicate to polypropylene is reduced thermal expansion, and, as a result, reduced shrinkage. At 4-6 wt. % loading
coefficient of linear thermal expansion (CLTE) and mold shrinkage are reduced by 10-20%. This reduction is beneficial since it minimizes mold dimension changes caused by changing polymer system\textsuperscript{61, 107}.

2.2.3.4 Flame retardancy

The flame retardant properties of nanocomposites have been very recently reviewed in detail by Gilman\textsuperscript{108}. The main bench-scale method used to measure important parameters in the flame retardant behavior of a material (heat release rate, peak of heat release rate, heat of combustion) is Cone calorimetry. In a typical experiment, the sample is exposed to a given heat flux (often taken as 35 kW/m\textsuperscript{2}) and the heat release rate (HRR) as well as the mass loss rate are recorded as a function of time. It is worth noting that reduction of the peak HRR is the most clear-cut evidence for the efficiency of a flame retardant. Moreover, gas and soot production are also measured. Cone calorimetry experiments have been carried out on intercalated PP (2 wt.%).

A significant decrease in the peak HRR is recorded while the heat of combustion, smoke and the carbon monoxide yields (other important properties in flammability concern) are usually not increased. These data tend to demonstrate that the improvement in flame retardancy does not occur by a process in the gas phase but rather by a modification of the combustion process in the condensed phase.

Experiments carried out in a radiative gasification apparatus\textsuperscript{109} have allowed to determine that the flame retardant effect of nanocomposites mainly arises from the formation of char layers obtained through the collapse of the exfoliated and/or
intercalated structures. This multilayered silicate structure may act as an excellent insulator and mass transport barrier, slowing down the escape of the volatile decomposition products\textsuperscript{110}. Whatever the nature of the matrix (thermoplastics or thermosets) and whatever the structure of the nanocomposite (exfoliated or intercalated), always the same interlayer spacing (13 Å) was found for the recovered chars as analyzed by XRD, implying the formation by combustion of a residue of the same nature.

2.2.3.5 Rheological properties

It is instructive to study the rheology of polymer/clay hybrids for two reasons. First, rheological properties are indicative of melt-processing behavior in unit operations such as injection molding. Second, since the rheological properties of particulate suspensions are sensitive to the structure, particle size, shape, and surface characteristics of the dispersed phase, rheology potentially offers means to assess the state of dispersion of nanocomposites directly in the melt state. Thus, rheology can be envisaged as a tool that is complementary to traditional methods of materials characterization such as electron microscopy, X-ray scattering, dynamic mechanical analysis, and mechanical testing. The advantages of rheology relative to these methods are that measurements are performed in the melt state and that a battery of different rheological methods can be used to study the response of the nanocomposite structure to both linear and nonlinear deformation. A disadvantage of rheological methods is that they probe the hybrid structure only indirectly; however, the distinctive features of nonlinear measurements and the sensitivity of linear viscoelasticity to surfactant chemistry demonstrate that such
methods can provide a useful characterization of nanocomposite structure, particularly at the mesoscopic level\textsuperscript{30}.

An addition of montmorillonite to PP causes pseudo-solid-like behaviors and slower relaxation behaviors of PP/clay melts. The dependence of $G'$ and $G''$ on $\omega$ shows nonterminal behavior with power-law dependence of $G'$ and $G''$, and it is much smaller than the expected\textsuperscript{111}.

The steady shear viscosities of PP/clay are much higher than those of pure PP at lower shear rate. At high shear rate, however, shear viscosities of the nanocomposites are comparable with or even lower than that of pure PP as a result of the preferential orientation of monmorillonite layers. Therefore, PP/clay composites have higher moduli but better processibility compared with pure PP\textsuperscript{111}.

Rheological approach was used to study kinetics of polypropylene melt intercalation into galleries of monmorillonite\textsuperscript{112}. By recording the change of viscoelastic response to small amplitude oscillatory shear, it was found that the increasing of intercalated tactoids detached from the primary particles resulted in the continuous enhancement of low-frequency modulus and viscosity and the formation of the percolation networks. The development of the relative volume fraction of intercalated tactoids was obtained from the rheological parameters of viscosity and storage modulus, which could be used to determine the apparent diffusivities for mass transport into the primary particles at the different temperatures. The activation energy of melt intercalation was found to be about 80±6 kJ/mol.
2.3 Modeling of melt intercalation of modified montmorillonite

The development of nanocomposite technology presents many scientific challenges. A better fundamental understanding, the ability to make predictions, are very important in accelerating the development of this technology. In particular, theory and simulations are especially useful in addressing thermodynamics and kinetics of exfoliation. This challenge is at the heart of the development of nanocomposite technology. Both the processing characteristics of the suspensions of clay platelets in polymers and the final properties of the fabricated articles made from these suspensions depend on the exfoliation and dispersion of the platelets. There is a significant amount of ongoing research in this area\textsuperscript{113-117}.

2.3.1 Lattice-based mean field theory

The thermodynamics that drives the intercalation of a polymer inside a modified layered silicate while the polymer is in the molten state has been approached through a lattice-based mean field theory by Vaia and Giannelis\textsuperscript{113}. They found that, in general, the outcome of polymer intercalation is determined by an interplay of entropic and enthalpic factors. In fact, although the confinement of the polymer chains inside the silicate galleries results in a decrease in the overall entropy of the macromolecular chains, this entropic penalty may be compensated by the increase in conformational freedom of the tethered alkyl surfactant chains as the inorganic layers separate, due to the less confined environment.
Since small increases in the gallery spacing do not influence strongly the total entropy change, intercalation will rather be driven by the changes in total enthalpy. In this study, the enthalpy of mixing has been classified in two components: apolar interactions generally unfavorable and arising from interaction between polymer and surfactant aliphatic (apolar) chains, and polar interactions which originate from the Lewis acid/Lewis base character of the layered polar silicates interacting with the polymer chains. Indeed, since in most conventional organo-modified silicates, the tethered surfactant chains are apolar, dispersion forces dominate polymer-surfactant interactions. On the other hand, a favorable energy decrease is associated with the establishment of many favorable polymer surface polar interactions. The enthalpy of mixing can thus be rendered favorable by maximizing the magnitude and number of favorable polymer-surface interactions while minimizing the magnitude and number of unfavorable apolar interactions between the polymer and the aliphatic chains introduced along the modified layer surfaces.

The free energy curves may be grouped into three types. First, curves that are positive at all gallery heights (type I). In this case, polymer intercalation is unfavorable, and the polymer and the organo-modified layered silicates are immiscible. The second type regroups the curves displaying one minimum (type IIa) or more than one minimum (type IIb) and corresponding, respectively, to well defined intercalated structure and ill-defined intercalated structures or intermediate intercalated structures before complete layer exfoliation. Finally, the third type of curves displays a continuous decrease in the free energy values with gallery height expansion (type III) indicating that polymer

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intercalation and complete layer separation is favorable. This last type corresponds to complete polymer-silicate layer miscibility, characteristic of exfoliation.

2.3.2 Self-consistent field theory

Balazs et al.\textsuperscript{114, 115} have considered the self-consistent field theory (SFC) in order to investigate the factors promoting the penetration of polymers into layered silicates. They first varied properties related to the nature of the tethered surfactant chains. They found out that an increase in the surfactant length (approaching the length of the polymer chains) improves the layers separation by the formation of a broad interface (or interphase) which prevents the polymer from adopting more conformational degrees of freedom. Accordingly, exfoliated or intercalated structures can be formed even for slightly unfavorable interactions between the polymer and the modified surfaces. On the opposite side, increase in the length of polymer chains tends to render the interlayer mixture immiscible. These authors also reported on the effect of the surfactant density on the intercalation process, showing that excessive density of tethered alkyl chains can impede the formation of intercalated structures.

2.3.3 The Onsager model

In order to model the macroscopic phase behavior of the polymer/clay mixture, Balazs et al.\textsuperscript{115, 116} have adapted the Onsager model developed for the equilibrium behavior of rigid rods dispersed in a polymer matrix. From this new model, one can calculate phase diagrams of the polymer/clay composites as a function of the Flory-
Huggins interaction parameter. These diagrams can differentiate immiscible and miscible regions further separated in isotropic or nematic (relatively ordered) arrangement. In this study, the blend miscibility appears to be strongly negatively influenced by an increase in the length of polymer chains. For very high polymer length, the particle/polymer mixture gets immiscible even for negative values of the interaction parameter. The phase diagram appears to be also strongly dependent upon the aspect ratio of the particle (i.e. the diameter (D) to thickness (L) ratio of the assumed disk-shaped particle).

The nematic ordering of disks is promoted by an increase in the diameter (asymmetry) of the disks. Note that, in the two limiting cases of low and high $D$, there is the possibility of isotropic-isotropic (i-i) phase coexistence in the former case and nematic-nematic (n-n) phase coexistence in the latter case.

2.3.4 Perturbation-type density functional theory

Ginzburg and Balazs$^{117}$ have developed an even more complex model, based on perturbation-type density functional theory to describe the complete (isotropic, nematic, smectic A, columnar and intercalated called 'crystalline') phase diagram of an incompressible polymer-disk mixture. The phase diagram is shown to be strongly dependent upon the shape anisotropy of the filler particles, the polymer chain length, and the strength of the inter-particle interaction. For instance, an increase in the inter-particle interaction strength leads to the complete disappearance of the nematic phase in favor to direct coexistence between isotropic and columnar or 'crystalline' (intercalated) structure.
2.4 Modeling of nanocomposites’ properties

Over several decades theoretical frameworks have been developed for predicting properties of composite materials based on the properties of the pure components and the morphology of the composite. An assumption inherent in all of these theories is that each component of the composite acts independently of the other. While the general objective of such theories is to predict performance of the composite for given set of components, these theories enable a simple route for evaluation of the individual contribution of component properties such as matrix and filler modulus, volume fraction, filler aspect ratio, filler orientation, etc. Aspect ratio is an important factor in polymer nanocomposites and drives an interest in achieving a high level of platelet exfoliation.

2.4.1 The composites theories

There are two well known composite theories of Halpin-Tsai and Mori-Tanaka. The two theories differ in regard to their treatment of filler geometry; however, they both show analogous responses to how composite modulus responds to filler aspect ratio, modulus, and orientation.

2.4.1.1 Halpin-Tsai theory

Halpin and Tsai developed a well known composite theory for predicting the stiffness of unidirectional composites as a function of aspect ratio\textsuperscript{118-120}. This theory is based on the early micromechanics works of Hermans\textsuperscript{121} and Hill\textsuperscript{122}. Hermans generalized the form of Hill’s self-consistent theory by considering a single fiber encased
in a cylindrical shell of matrix, that is embedded an infinite medium assumed to possess the average properties of the composite. Halpin and Tsai reduced Hermans’ results into a simpler analytical form adapted for a variety of reinforcement geometries, including discontinuous filler reinforcement. The longitudinal and transverse engineering moduli, $E_{11}$ and $E_{22}$; are expressed in the general form

$$
\frac{E}{E_m} = \frac{1 + \zeta \eta \phi_f}{1 - \eta \phi_f} \tag{2.1}
$$

where $E$ and $E_m$ represent the Young’s modulus of the composite and matrix, respectively, $\zeta$ is a shape parameter dependent upon filler geometry and loading direction, $\phi_f$ is the volume fraction of filler, and $\eta$ is given by

$$
\eta = \frac{E_f / E_m - 1}{E_f / E_m + \zeta} \tag{2.2}
$$

where $E_f$ represents the Young’s modulus of the filler. By comparing model predictions with the two-dimensional finite element calculations of Foye\textsuperscript{123} for discontinuous oriented square fiber-reinforced composites, Ashton et al.\textsuperscript{120} determined that $\zeta=2(a/b)$ provided good agreement for longitudinal modulus; where $a$ and $b$ are the length and thickness of the fiber. The modulus perpendicular to the fiber direction (transverse), on the other hand, was found to be relatively insensitive to fiber aspect ratio, and could be approximated by $\zeta=2$ \textsuperscript{120, 123}. It should be noted that as $\zeta\to0$ the Halpin–Tsai theory converges to the inverse rule of mixtures (lower bound), i.e.

$$
\frac{1}{E} = \frac{\phi_f}{E_f} + \left(1 - \phi_f\right) \frac{1}{E_m} \tag{2.3}
$$
Conversely, when $\zeta \to 0$ the theory reduces to the rule of mixtures (upper bound), i.e.

$$E = \phi_f E_f + \left(1 - \phi_f\right) E_m$$  \hspace{1cm} (2.4)$$

Furthermore, the Halpin–Tsai equations retain the same form for discontinuous cylindrical fibers and lamellar shape reinforcements, such as ribbons or rectangular platelets; however, when calculating elastic moduli $E_{11}$ and $E_{22}$ in the case of ribbons or rectangular platelets, $\zeta$ is equal to ($l/t$) and ($w/t$); respectively, where $l$ is the length, $w$ is the width, and $t$ is the thickness of the dispersed phase.

2.4.1.2 Mori-Tanaka theory

The Mori–Tanaka average stress theory has also received considerable attention in the literature\textsuperscript{125}. It was derived on the principles of Eshelby’s inclusion model for predicting an elastic stress field in and around an ellipsoidal particle in an infinite matrix\textsuperscript{126}. To account for finite filler concentrations, Mori and Tanaka\textsuperscript{125}, however, considered a non-dilute composite consisting of many identical spheroidal particles that cause the matrix to experience an average stress different from that of the applied stress; to satisfy equilibrium conditions the volume average over the entire composite was forced to equal the applied stress. Tandon and Weng\textsuperscript{127} used this assumption and Eshelby’s solution to derive complete analytical solutions for the elastic moduli of an isotropic matrix filled with aligned spheroidal inclusions. Their results for longitudinal and transverse elastic moduli are

$$\frac{E_{11}}{E_m} = \frac{A}{A + \phi_f \left(A_l + 2\nu_m A_t\right)}$$  \hspace{1cm} (2.5)$$
and

\[
\frac{E_{22}}{E_m} = \frac{2A}{2A + \phi \left[ -2\nu_0 A_3 + (1 - \nu_m) A_4 + (1 + \nu_m) A_5 A \right]},
\]

(2.6)

where \( \phi \) is the volume fraction of filler, \( \nu_0 \) is the Poisson’s ratio of the matrix, and \( A_1, A_2, A_3, A_4, A_5 \) and \( A \) are functions of the Eshelby’s tensor and the properties of the filler and the matrix, specifically Young’s modulus, Poisson’s ratio, filler concentration and filler aspect ratio; complete details of these equations are given elsewhere. It is important to note that the composite moduli in the equations are dependent upon the shape of the filler, e.g. fiber-like versus disk-like ellipsoids, which are accounted for in the Eshelby’s tensor.

A number of assumptions are inherent to both approaches; the filler and matrix are linearly elastic, isotropic, and firmly bonded. The filler is perfectly aligned, asymmetric, and uniform in shape and size. Particle–particle interactions are not explicitly considered. Of course, for all composite theories the properties of the matrix and filler are considered to be identical to those of the pure components. In addition to these assumptions, there are number of differences between the two theories that are worth noting. First, the Mori–Tanaka theory treats fibers and disks as ellipsoidal particles, whereas the Halpin–Tsai equations treat a fiber as a fiber and disk as a rectangular platelet; the later disparity in the Halpin–Tsai equations is of some concern, since the length and, in turn, aspect ratio across a disk is not constant. Second, the Halpin–Tsai equations for \( E_{11} \) and \( E_{22} \) are independent of the Poisson’s ratio of the filler or the matrix. Third, the Halpin–Tsai equations for the transverse modulus, i.e. perpendicular to the filler’s major axis, are independent of aspect ratio.
Last, it is important to emphasize that numerous complexities arise when comparing composite theory to experimental composite data, particularly for polymer layered silicate nanocomposites. In addition to physical disparities between theory and experiment, the choice of composite theory will also dictate how well the predicted and observed properties agree\textsuperscript{128}.

2.4.2 Micromechanics of nanocomposites

Nanocomposite mechanics is not yet well-understood. It has been addressed by developing analytical solutions for the elasticity equations, what are considered to be the three most important aspects of the micromechanics of nanocomposites reinforced by platelet-shaped fillers. Micromechanical methods use simplified geometries, thus neglecting complex geometrical features which could potentially be taken into account in numerical solutions of the elasticity equations by finite element simulations. They assume perfect adhesion (perfect load transfer) between the components in a composite, thus also neglecting interfacial phenomena, which could potentially be taken into account by mesoscale simulations. Nonetheless, they are extremely useful. Since the calculations are instantaneous, they provide the ability to assess rapidly the key factors controlling the elastic behavior and to explore very large design spaces\textsuperscript{129}.

2.4.2.1 Comparison of tensile and compressive elastic moduli

Although dispersed clay platelets have a very high intrinsic stiffness (tensile moduli of $\sim 10^5$ MPa), their high aspect ratios induce large bending moments so that they
manifest considerable flexibility\textsuperscript{130}. Will composite using fillers of high aspect ratio exhibit an enhanced compressive modulus in addition to an enhanced tensile modulus? To answer this question a model was developed to predict the buckling of platelets in reinforced materials under compressive loading. This model predicts a critical strain above which platelet buckling, and hence a reduction in the compressive modulus relative to the tensile modulus, would be expected to occur.

\[
e_{\text{crit}} = \frac{G_{\text{matrix}}(1 - \phi)}{E_{\text{filler}} \phi} = \left( \frac{E_{\text{matrix}}}{E_{\text{filler}}} \right) \left( \frac{1}{2(1 + \nu_{\text{matrix}})} \right) \left( \frac{1 - \phi}{\phi} \right)
\]

(2.7)

where \( G_{\text{matrix}} \) is the matrix shear modulus, \( E_{\text{matrix}} \) is the filler Young’s modulus, and \( \phi \) is the volume fraction filler. This formula was used in calculations on a typical polypropylene nanocomposite, for which the compressive modulus was not reduced relative to the tensile modulus\textsuperscript{129}.

2.4.2.2 Effect of incomplete exfoliation on modulus

It is obvious from electron micrographs that one often has incompletely exfoliated stacks of platelets, containing some organocation and/or matrix polymer between the platelets in each stack. Such stacks can contain several platelets, and the platelets within a stack can be at various distances from each other. An important issue, which may have drastic effects on the reinforcement efficiency, is the point in the interlayer expansion of a stack with a given number of layers at which a stack becomes a collection of separate exfoliated platelets of high aspect ratio of \( A_f \) and Young's modulus of \( E \) at a volume fraction of \( \phi \), rather than behaving like a single 'pseudoparticle'. A
pseudoparticle would have a lower 'effective' aspect ratio $A'_f$ (because of stacking), and a lower Young's modulus $E'$ as well as a higher volume fraction $\phi'$ (because of its trapped organic fraction). A standard technique of composite theory that is used routinely to estimate reinforcement effects, the Halpin-Tsai equations\textsuperscript{119}, was modified to account for these effects\textsuperscript{129}. The resulting set of equations is:

\[ \frac{E_{\text{composite}}}{E_{\text{matrix}}} = \frac{1 + 2A'_f\eta'\phi'}{1 - \eta'\phi'}, \quad \eta' = \frac{E'_r - 1}{E'_r + 2A'_f} \]  

(2.8)

\[ A'_f = \frac{A_f}{N} \left( \frac{1}{1 + \left(1 - \frac{N}{\hat{N}}\right)^S} \right) \]  

(2.9)

\[ \phi = \phi \left(1 + \left(1 - \frac{N}{\hat{N}}\right)^S\right) \]  

(2.10)

\[ E'_r = E'_r \left( \frac{1}{1 + \left(1 - \frac{N}{\hat{N}}\right)^S} \right) + \frac{\left(1 - \frac{N}{\hat{N}}\right)^S}{1 + \left(1 - \frac{N}{\hat{N}}\right)^S} \]  

(2.11)

\[ \hat{N} = N + (1 - N)\left(\frac{S}{t}\right)^{\phi \left(\frac{\phi}{1 - \phi}\right)} \]  

(2.12)

where $E'_r$ is the ratio of the modulus of the platelet stack to that of the matrix, $A'_f$ is the effective aspect ratio, $N$ is the number of platelets per stack, and $s/t$ is the ratio of platelet spacing to platelet thickness in stack.

This model accounts for the reduction of the reinforcement efficiency of clay platelets of high aspect ratio in a polymer matrix as a result of the incomplete exfoliation of platelets into 'pseudoparticle' stacks containing polymer layers sandwiched between successive clay platelet layers rather than into individual perfectly exfoliated and well-
dispersed platelets. It was shown that incomplete exfoliation has a very significant detrimental effect on the reinforcement efficiency\textsuperscript{129}.

2.4.2.3 Effect of imperfect alignment on modulus

Incomplete exfoliation is just one of the two separate important effects which, in combination, significantly lower the reinforcement efficiency observed in typical nanocomposites relative to the ultimate theoretical limits. A model was also developed for the other important effect, which is the deviation of the platelet orientation from perfect biaxial in-plane. It was shown by detailed calculations using that the deviation of the platelet orientation from perfect biaxial in-plane also has a very significant detrimental effect on the reinforcement efficiency\textsuperscript{129}.

Authors predicted Young's modulus as a function of the angle between the applied normal stress and the symmetry axis of the platelets. They were able to predict the response of Young's modulus of a nanocomposite material to changes in the direction of the applied normal stress. The results show that (a) platelet orientation has a significant effect on Young's modulus, and (b) a minimum value of Young's modulus exists when the particle symmetry axis is about 40° away from the applied normal stress\textsuperscript{129}.

2.5 Ultrasound

2.5.1 Ultrasound basics

Ultrasound can be defined as sound with a frequency above the threshold of human hearing (i.e. >20 kHz). The range of human hearing is from about 20 Hz to 20
kHz. The upper limit of ultrasonic frequency is not sharply defined but is usually taken to be 5 MHz for gases and 500 MHz for liquids and solids.

The uses of ultrasound within this large range may be divided broadly into two areas. The first area involves low amplitude (higher frequency) sound and is concerned with the physical effect of medium on the wave and is commonly referred to as “low power” or “high frequency ultrasound”. Typically, low amplitude waves are used for analytical purpose to measure the velocity and absorption coefficient of the wave in a medium in the 2 to 10 MHz range. Information from such measurement can be used in medical imaging, chemical analysis and the study of relaxation phenomena.

The second area involving high energy (low frequency) waves, known as “power ultrasound”, and lies between 20 and 100 kHz. It is used for cleaning, plastic welding and, more recently, for sonochemistry. In fact the range available for sonochemistry has been extended to 2 MHz with the development of high power equipment capable of generating cavitation within liquid systems at these high frequencies\textsuperscript{131}.

In a longitudinal wave the disturbance moves parallel to the direction of propagation; in a transverse wave the disturbance moves perpendicular to the direction of propagation. Sound wave is longitudinal.

2.5.2 Acoustic cavitation

Sound waves pass through liquids as alternating series of longitudinal compressions and rarefactions causing a variation in pressure. As schematically shown in Figure 16, the acoustic pressure can vary over several bars. If the intensity is sufficiently
high, the negative pressure can overcome the attractive forces between the molecules of the liquid resulting in the formation of a cavity or bubble, particularly if dissolved gas or suspended solid particles can act as nucleating sites. Solvent vapor and/or dissolved gases can enter the bubble, preventing its complete collapse during the rarefaction cycle. The process continues and the bubble grows until it reaches a size in the region of 100-200 μm at which it comes into resonance with the sound field and undergoes a rapid expansion and collapse\textsuperscript{132}.

On the assumption that the bubble collapse, which occurs on a microsecond timescale adiabatically, Noltlink and Neppiras\textsuperscript{133} showed that the final temperatures and pressures generated, are 1000-2000 bar and 4000-6000 K.

There is now considerable experimental evidence to support these theoretical calculations in the so-called ‘hot spot’ theory\textsuperscript{134}. The spectra of species, which arising from sonoluminescence where short flashes or light are emitted during cavitation, from alkane solvents are very similar to those from species involved in combustion at several thousand Kelvin. However Margulis\textsuperscript{135} has shown that there are some phenomena which are better explained by an alterative ‘electrical’ theory. This considers the charge distributions due to dipoles and their alignment around a cavitation bubble.

Although the precise origin of cavitation is not clear yet, it is certain that cavitation serves as a means of concentrating the diffuse energy of sound into a unique set of conditions to produce unusual materials from dissolved precursors. It is the energy changes involved in this process that provides the source of activation for chemical reactions.
2.5.3 Sonochemistry

Sonochemistry, like thermochemistry, piezochemistry, is about the study of ultrasonic effects in chemistry. High-intensity ultrasound can induce a wide range of chemical and physical consequences. The chemical effects of ultrasound include homogenous sonochemistry of liquids, heterogeneous sonochemistry of liquid-liquid or liquid-solid systems, and sonocatalysis. Applications of ultrasound to materials chemistry are found in all of these categories. Physical effects of high-intensity ultrasound, which often have chemical consequences, include enhanced mass transport, emulsification, bulk thermal heating, and a variety of effects on solids.

The chemical consequences of high-intensity ultrasound do not arise from the interaction of acoustic waves and matter at a molecular or atomic level. Instead, in liquids irradiated by high-intensity ultrasound, acoustic cavitation provides the primary mechanism for sonochemical effects\textsuperscript{136}.

2.5.4 Effects of ultrasound on polymers

The effects of ultrasound on polymers can be both physical and chemical. Irradiation of liquids with ultrasound can cause solely physical changes from acoustic streaming, such as rapid mixing and bulk heating. Although cavitation is not always necessary for these effects, they almost always accompany cavitation. Examples of physical changes induced by ultrasound in polymer systems include the dispersion of fillers and other components into base polymers, the encapsulation of inorganic particles with polymers, modification of particle size in polymer powders, the welding of

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thermoplastics, polymer processing. In contrast, chemical changes can also be created during ultrasonic irradiation, invariably as a result of cavitation\textsuperscript{136}.

2.5.4.1 Sonochemical synthesis of polymers

As cavitation can produce high concentrations of radicals, hence, application of ultrasound to monomers (e.g. \( \alpha \)-olefins and vinyl) provides an alternative, highly controllable method of initiation.

The primary role of ultrasound is to produce the radicals needed to initiate polymerization\textsuperscript{136}. In addition, higher temperature led to an increase in the rate of polymerization. In emulsion polymerization, the large degree of motion induced by acoustic streaming and cavitation shockwaves creates very high shear forces, which improve emulsification\textsuperscript{137}.

2.5.4.2 Ultrasonic degradation of polymer in solution

In 1930s, the degradation of polymers in solutions by ultrasound was first reported\textsuperscript{138}. Numbers of studies have been carried out over the past few decades\textsuperscript{132, 136}. It is noted that the degradation proceeds more rapidly at higher molecular weights and approaches a limiting value, \( M_{\text{lim}} \), below which no further degradation takes place\textsuperscript{139}.

In this process, polymer chains are subjected to extremely large forces in the rapid liquid flows near collapsing cavitation bubbles and in the shock waves generated after bubble implosion, which can result in the breakage of a bond in the polymer chain.
The difference of ultrasonic degradation from thermal degradation is the loci of the chain scission. Thermal degradation produces cleavage at random point along the chain, while ultrasonic degradation is much more specific, with cleavage occurring preferentially near the middle of the chain\textsuperscript{140, 141}.

2.5.4.3 Ultrasonic devulcanization of rubbers

The first works reported about the effects of ultrasound on polymer melts were carried out in the 1970s in the USSR. Isayev and his coworkers have carried out extensive studies on ultrasonic devulcanization of various vulcanizates, including ground tire rubber (GRT)\textsuperscript{142}, styrene-butadiene rubber (SBR)\textsuperscript{143-147}, natural rubber (NR)\textsuperscript{148,149}, silicone rubber\textsuperscript{150, 151}, and rubber/rubber blends\textsuperscript{152}. Ultrasonic waves of certain levels in the presence of pressure and heat can break down the three dimensional network in crosslinked rubbers. Devulcanized rubber can be reprocessed in the very much the same way as virgin rubbers. The process of ultrasonic devulcanization is very fast, occurring in about a second, and may lead to a preferential breakage of sulfidic crosslinks in vulcanized rubbers.

2.5.4.4 Compatibilization of polymer blends by ultrasonic treatment

During the ultrasonic treatment of polymers, degradation takes place due to chain scission. And it was also observed when polymer solutions are subjected to exposure of high intensity ultrasound waves, stresses induced by cavitation leads to hemolytic cleavage of polymer chains, and consequently causing the molecular weight
decrease\textsuperscript{153}. It is also known that long-chain polymer molecules can be ruptured by high intensity ultrasound during melt extrusion\textsuperscript{69}. The breakage of the C-C bond by ultrasound usually leads to formation of long-chain radicals\textsuperscript{70}. In polymer blends, radicals from two different polymers may combine with the formation of block copolymers. Recently, enhanced compatibilization of polymer blends by ultrasound treatment was reported\textsuperscript{154-158}. PE/PS\textsuperscript{157}, PP/PS\textsuperscript{158} blends were treated by ultrasound, and it was claimed that in-situ compatibilization was realized through the mechanism mentioned above.

2.5.4.5 Application of ultrasound in nanocomposite preparation

Several studies about application of ultrasound in nanocomposite preparation were published within last three years. One of them was on preparation and characterization of nickel-polystyrene nanocomposite\textsuperscript{71}, the second one was on preparation of conductive polyaniline-nanosilica particle composites\textsuperscript{72}, the third one had described silica agglomerate breakdown in continuous ultrasonic extruder\textsuperscript{73, 74}. They all claim that ultrasound may assist in better filler dispersion. Finally, an attempt to develop polypropylene-clay nanocomposite via melt intercalation in intensive batch mixer equipped with powerful ultrasound was reported\textsuperscript{75}. 

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CHAPTER III
EXPERIMENTAL

3.1 Materials

Poly(propylene) (PP) (melt flow index 4.0 dg/min at 230°C, density 0.9 g/cm³, and $M_w=351,000$), made by Basell North America Inc. (Elkton, MD) under trade name Pro-fax® 6523.

High density poly(ethylene) (HDPE) (melt flow index 5.0 dg/min at 230°C, and density 0.9 g/cm³), made by Chevron Phillips under trade name Marlex® HMN 4550.

The maleated PP (PP-MA) used in this study was Polybond® 3002 with maleic anhydride level of 0.2 weight % and MFI of 7 dg/min which was kindly supplied by Crompton.

Cloisite® 15A and Cloisite® 20A are natural montmorillonites (MMT) modified with a quaternary ammonium salt. They serve as additives for plastics to improve various plastic physical properties, such as reinforcement, HDT, CLTE and barrier. Properties of the selected MMTs are listed in Table 3.1.
Table 3.1 Typical properties of Cloisites (as specified by the manufacturer)

<table>
<thead>
<tr>
<th>Treatment/Properties:</th>
<th>Organic Modifier (1)</th>
<th>Modifier Concentration</th>
<th>% Moisture</th>
<th>% Weight Loss on Ignition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloisite® 20A</td>
<td>2M2HT</td>
<td>95 meq/100g clay</td>
<td>&lt; 2%</td>
<td>38%</td>
</tr>
<tr>
<td>Cloisite® 15A</td>
<td>2M2HT</td>
<td>125 meq/100g clay</td>
<td>&lt; 2%</td>
<td>43%</td>
</tr>
</tbody>
</table>

\[
\text{CH}_3 \quad \text{CH}_3 \quad \text{N}^+ \quad \text{HT} \\
\text{N}^+ \quad \text{HT} \\
\]

Where HT is hydrogenated tallow (~65% C18; ~30% C16; ~5% C14) noted as 2M2HT: dimethyl, dehydrogenated tallow, quaternary ammonium. Anion: Chloride

Dry particle sizes for both Cloisites (microns, by volume).

<table>
<thead>
<tr>
<th>10% less than:</th>
<th>50% less than:</th>
<th>90% less than:</th>
</tr>
</thead>
<tbody>
<tr>
<td>2µ</td>
<td>6µ</td>
<td>13µ</td>
</tr>
</tbody>
</table>

Color: Off White

Density and X Ray Results.

<table>
<thead>
<tr>
<th></th>
<th>Loose Bulk, lbs/ft³</th>
<th>Packed Bulk, lbs/ft³</th>
<th>Specific Gravity, g/cc</th>
<th>X Ray Results d₀₀₁, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloisite® 20A</td>
<td>7.35</td>
<td>13.55</td>
<td>1.77</td>
<td>24.2</td>
</tr>
<tr>
<td>Cloisite® 15A</td>
<td>10.79</td>
<td>18.64</td>
<td>1.66</td>
<td>31.5</td>
</tr>
</tbody>
</table>
3.2 Preparation of nanocomposites

3.2.1 Two stages process

At the first stage a co-rotating twin screw extruder (JSW Labotex 30) was used to compound PP and clay at 55 g/min feed rate. Screw configuration is shown in Figure 3.1. Screw speed was set at 240 rpm and zone temperatures of 100/190/180/180/175/175/175/190 ºC were used. The melt temperature varied from 195 to 200 ºC. Die pressure and power consumption were measured. The extrudates were water-cooled and pelletized.

At the second stage the material was treated by ultrasound in molten state. In the ultrasonic treatment reactor (Figure 3.2(a)), two water-cooled horns of square cross sections of 38.1×38.1 mm² were placed in a slit die of rectangular cross sections with dimensions of 157.5×38.1×4.0 mm³ (Figure 3.2(b)), which was attached to a 25.4 mm plastic extruder (Killion, L/D = 24) with screw configuration shown in Figure 3.2(c). A shaping die having 4 holes of diameter of 3.175 mm was attached to the end of the slit die. Tap water flow rate of 3500 cm³/min was used and controlled by flow meter (Key Instruments). Two pressure transducers (Dynisco, PT465XL) of maximum pressure of 51.7 MPa and 34.5 MPa were placed in the slit die before and after the treatment zone at distances of 21.6 mm from the front and end of the horn. A drawing of the reactor is shown in Figure 3.2(a). A pair of a 3.3 kW ultrasonic power supply (Branson Ultrasonics Corp., 2000bde), a converter (Branson Ultrasonics Corp., CR-20), and 1:1 booster (Branson Ultrasonics Corp) provide the longitudinal vibrations of the horn with a frequency of 20 kHz. Amplitude of 10 µm was used at 55 % of maximum power as
shown in Figure 3.3. Three different flow rates of the material were realized to vary residence time.

3.2.2 Single stage process

The ultrasonic treatment reactor has been modified for single-stage process. Namely, the original screw depicted in Fig. 3.2(c) was replaced by a screw with mixing elements (Figure 3.4) that allowed carrying out ultrasonic treatment of polyolefin/clay immediately after compounding stage. Design of the screw included standard Maddock mixer and Melt Star mixer. Processing was performed using temperature settings in 4 zones and die of 180/200/200/200/200 °C. Two regimes of feeding were applied, namely, starved (screw speed of 100 rpm) and flood feeding (screw speed variable). The ultrasonic treatment was carried out at a frequency of 20 kHz and two horns. Gap size of 2 mm and 4 mm were used in addition to three different flow rates of the material (0.25, 0.5, and 0.75 g/s) to vary residence time. This single stage process minimized degradation of PP matrix.

3.2.4 Molding

3.2.4.1 Compression molding

The obtained polyolefin/clay composites were compression molded into disks (diameter of 25 mm and 2 mm thick) for 5 minutes at a temperature of 200 °C and at a pressure of 24 MPa in an electrically heated compression molding press (Carver 4122).
The molded samples were cooled in water bath and used further for rheological measurements.

The samples for XRD measurements were obtained by the same technique. The final shape was a 0.5 mm sheet.

Thin films (20 mils) for oxygen permeability test were compression molded at the conditions mentioned above. The only difference is that they were left pressurized until they reach room temperature to avoid warpage.

3.3.4.1 Injection molding

The pellets of polyolefin/clay materials are injection molded in a Van Dorn 55 HPS 2.8F injection molding machine to obtain dog bone shaped samples for tensile testing and rectangular bars for impact test. The process parameters are listed in Table 3.2.

3.3 Characterization

3.3.1 Morphological studies

3.3.1.1 X-Ray Diffraction (XRD)

Using a Rigaku X-ray machine with wavelength $\lambda = 1.54$ Å operated at 40 kV and 150 mA, X-ray diffraction patterns were obtained to determine the mean interlayer spacing of the (001) plane ($d_{(001)}$) for the organoclays and its nanocomposites with polymers. The scanning range was varied form $2\Theta = 1.5^\circ$ to $10^\circ$ with increment of $0.02^\circ$ and fixed time of 5 s in reflection mode.
Figure 3.1 Screw element configuration of JSW 30
Figure 3.2 Schematic drawing of the ultrasonic treatment reactor
Figure 3.3 Amplitude calibration plot.
Figure 3.4 Photo of the screw (a) with mixing elements (b).
Table 3.2 Injection molding conditions.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Nozzle</th>
<th>Front</th>
<th>Center</th>
<th>Rear</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Barrel</td>
<td>200</td>
<td>200</td>
<td>190</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Injection Pressure, MPa</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hold pressure, MPa</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Injection speed, mm/s</td>
<td>38.1</td>
<td></td>
</tr>
<tr>
<td>Holding time, s</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>Cycle time, s</td>
<td>70</td>
<td></td>
</tr>
</tbody>
</table>
3.3.1.2 Transmission Electron Microscopy (TEM)

Morphological studies were carried out by transmission electron microscopy (TEM). The ultrathin sections of specimens were obtained by cryoultramicrotomy at T= -80 °C, below the glass transition temperature of polymeric matrix (-20 °C for PP and -30°C for HDPE), to attain the rigidity of the specimen, using a RMC Power Tome PC low-temperature sectioning system equipped with a diamond knife. Thin sections of specimen (ca. 50 nm) were transferred on a copper grid. A transmission electron microscopy (TECNAI 12, Philips) operated at 120 kV was used for taking pictures of the specimens.

3.3.1.3 Atomic Force Microscope (AFM)

Atomic force microscope (AFM) was used to study the morphology. AFM had been invented by Binnig et al. in 1986. The AFM technique allowed probing of nonconductive materials as well as conductive materials. The morphology of polymer blends has been studied by AFM.

The AFM probes the surface of a sample with a sharp tip several microns long terminating in a tip shorter than 10 nm in diameter is attached to a cantilever several hundred microns in length. In contact mode of this method shown in Figure 3.5, the tip is dragged across the surface (or the surface dragged under the tip). Van der Waals forces between the tip and the surface cause the cantilever to bend, and the extent of this cantilever deflection is measured. The measured cantilever deflections allow a computer to generate a map of surface topography.
The force most commonly associated with AFM is an interatomic force called the Van der Waals force. The dependence of the Van der Waals force upon the distance between the tip and the sample is shown in Fig. 3.6. In the contact regime, the cantilever is held less than a few angstroms from the sample surface, and the interatomic force between the cantilever and the sample is repulsive. In the non-contact regime, the cantilever is held on the order of tens to hundreds of angstroms from the sample surface, and the interatomic force between the cantilever and sample is attractive\textsuperscript{160}.

The cantilever bends as the tip is scanned across the surface due to these repulsive forces at different surface topologies. The bending of the cantilever is commonly sensed using an optical technique involving deflection of a laser beam reflected off of the cantilever as sensed by a position-sensitive photodiode. This arrangement is sensitive to 0.1 nm vertical displacement of the cantilever position.

Several modes of topographical imaging are determined by the type of tip scanning (Fig. 3.5). The first operational mode is called a contact mode, the AFM tip is dragging over a surface with a constant velocity and under constant normal mode. Scanning can be done in two different fashions: a height mode if the cantilever deflection is kept constant by the extending retracing piezoelement tube and a deflection mode if the piezotube extension is constant and the cantilever deflection is recorded.

A noncontact mode has been introduced to overcome the surface damage problems associated with the high local pressure. The basic idea of this dynamic mode (tapping mode) is replacing the instant tip surface contact with brief near-contact approachings of the oscillating tip (Fig. 3.5). The specially designed AFM tip oscillates

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with a high frequency close to its resonant frequency (usually, 200-300 kHz). In the vicinity of the surface, weak interactions can significantly change the amplitude of tip oscillations (amplitude detection) in response to surface topography and lead to a phase shift (phase imaging)\textsuperscript{161}. This mode of operation is useful, because it overcomes the potentially destructive effects of contact AFM due to the elimination of lateral forces experienced during dragging of the tip while still retaining sub-nm vertical resolution.

In this study, measurements were performed with a Nanoscope IIIa/Dimension 3000 (Digital Instruments) in the tapping mode at ambient conditions, using the electronic extender module allowing simultaneously the phase detection and height imaging. We used Si tips (Tap 300, Metrology Probes\textsuperscript{®}, Nano Devices) with a resonant frequency of about 300 kHz. Scan rates were between 0.2 and 4 Hz. The free oscillation amplitude $A_0$ of the oscillating cantilever was around 50 nm, the set point amplitude $A_{sp}$ (damped amplitude, when the tip was in intermittent contact) was slightly lower. Topographic (height mode) and viscoelastic (phase mode) data were recorded simultaneously under tapping conditions on the cryomicrotomed surface of polymer-clay nanocomposites. Phase images revealed hard regions in dark (the clay inclusions) and soft regions in bright (the polymer matrix).

3.3.2 Rheological properties

For rheological test at frequency sweep, the rotational rheometer ARES made by Rheometric was used. The diameter of the plate fixtures was 25 mm.
Figure 3.5 Different AFM scanning modes\textsuperscript{161}.
Figure 3.6 Interatomic force vs. distance curve$^{160}$. 

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The pellets were compression molded into a disk with diameter of 25 mm and thickness of 2 mm for test. The measuring range of frequency of ARES was from 0.03 to 100 s\(^{-1}\); strain remained constant at 4%. After zeroing fixtures (contact between the upper and lower plates and set the zero position) at the testing temperature 200 °C, the sample was inserted, and the gap size was gradually reduced to the 1.9 mm for dynamic tests by using configuration of parallel plates. Excess material flush was removed with aluminum tools, and the test started.

3.3.3 Mechanical properties

3.3.3.1 Tensile test

Tensile measurements of injection molded samples were performed according ASTM D 638-00 at room temperature on an Instron test machine, Model 5567. Tests were carried out at a crosshead speed of 50 mm/min with a 30 kN load cell without use of an extensometer. All the results were the average of five measurements.

From the recorded engineering stress-strain curves, the tensile strength, modulus were determined. The engineering tensile strength was defined as

\[
\sigma = \frac{F}{A_0}
\]

where, \(F\) is the force magnitude at rupture and \(A_0\) is cross-sectional area of the unstrained specimen. The elongation was defined as

\[
\varepsilon = \frac{l-l_0}{l_0} \times 100
\]
where, $\varepsilon$ is the elongation in percent of original gauge length $l_0$, $l$ is the observed length of the extended specimen.

3.3.3.2 Impact test

The unnotched Izod pendulum impact resistance was obtained by using injection molded standard bars with a notch according to ASTM D 256-00. The samples were hit from the backside of the notch. Five specimens were used and averaged results and error range were obtained. 22.241 N (5 lbs) pendulum was used. All tests were performed at room temperature.

3.3.4 Thermal properties

A Mettler Toledo Differential Scanning Calorimeter (DSC 821®) was used to determine heat flux and temperature at melting of the polymer/clay nanocomposites. The instrument was calibrated with indium. The experiments were run twice from 20 to 200 °C at the heating rate of 20°C/min under nitrogen atmosphere to eliminate any thermal history. The sample weight was about 5-10 mg.

Thermal gravimetric analysis (TGA) was performed on Mettler Toledo thermal analyzer, model TGA/SDT 851®, at 20°C/min heating rate, from 50 to 600°C under nitrogen atmosphere. Each time about 15 mg of sample was used.
3.3.5 Barrier Properties

Oxygen transmission rate (OTR) was measured by Illinois Instruments Oxygen Permeation Analyzer, Model 8000, according to ASTM D 3985-95. Compression molded films of 20 mils thick were used. A circle of 10 cm in diameter was cut from a film and placed in the chamber. Nitrogen and oxygen flows were set at 0.31 MPa. Purge level was set at 10 units. Each run was timed for 360 minutes.
CHAPTER IV

CONTINUOUS TWO STAGE PROCESS FOR MELT INTERCALATION OF PP-CLAY NANOCOMPOSITES WITH AID OF POWER ULTRASOUND

4.1 Introduction

In spite of the large number of studies on preparation of polypropylene-clay nanocomposites no direct intercalation of polymer in simple organically modified layered silicates has been observed due to polymeric matrix apolarity. Two different techniques are used to overcome this problem. The first one is functionalization of the polypropylene chain by either maleic anhydride or hydroxyl groups\textsuperscript{67}. In the second technique a commercially available organoammonium-exchanged montmorillonite is modified using an organic swelling agent in order to increase the interlayer spacing. The swollen organoclay is then compounded with polypropylene in a twin-screw extruder at 250°C. The swelling agent is volatilized during the extrusion process, leading to the formation of a nanocomposite\textsuperscript{68}. As one can see, both methods use additional chemicals, and, what is more, the second way is not environmentally friendly.

A number of studies of the effects of ultrasound on polymers have been performed and reported. It was observed that long-chain polymer molecules can be ruptured by high intensity ultrasound during melt extrusion\textsuperscript{69} leading to the formation of long-chain radicals\textsuperscript{70}. In polymer-filler systems, polymeric radicals may terminate on the clay surface
or combine with the surface modifying agent (in the case of organoclay) forming a chemical bond.

Several studies about the application of ultrasound in nanocomposite preparation were published within the last three years\textsuperscript{71, 72, 74}. These studies were devoted to preparation and characterization of nickel-polystyrene nanocomposites\textsuperscript{71}, conductive polyaniline-nanosilica particle composites\textsuperscript{72}, and silica agglomerate breakdown in a continuous ultrasonic extruder\textsuperscript{74}. They all found that ultrasound may assist in better filler dispersion. Finally, attempts to develop polymer/clay nanocomposites via melt intercalation in an intensive batch mixer\textsuperscript{75, 162, 163} and a stationary cup\textsuperscript{164} equipped with power ultrasound were reported. However, a prolonged ultrasonic treatment (10-20 mins) was used in these studies, apparently leading to a substantial degradation of polymer matrix.

With this in mind, the present study describes the effect of residence time of the polymer in the ultrasonic treatment zone on controlling the structure and properties of PP/clay nanocomposites. Rheological properties, morphology, and mechanical properties of the untreated and ultrasonically treated nanocomposites were investigated.

4.2 Experimental

4.2.1 First stage - compounding of nanocomposites

PP/clay nanocomposites with varying clay content of 2.5, 5.0, and 10.0 wt % were dry mixed and fed into a co-rotating twin screw extruder JSW Labotex 30 with screw
configuration depicted in Figure 3.1. The screw speed was set at 240 rpm to achieve high shear rate in the melt and zone temperatures of 100/190/180/180/175/175/175/190 °C were used. The extrudates were water-cooled and pelletized.

4.2.2 Second stage - ultrasonic treatment of PP/clay nanocomposites

The material was treated by ultrasound in the molten state. Two horns with 4 mm gap size and 10 μm ultrasound amplitude were used. The details of the ultrasonic treatment reactor were shown in Figure 3.2. Three different flow rates of the material (0.25, 0.5, and 0.75 g/s) were realized to vary residence time (21, 14, and 7 s, accordingly).

4.2.3 Molding

The pellets of PP/clay materials were injection molded in a Van Dorn 55 injection molding machine. The process parameters were listed in Table 3.2.

The obtained PP/clay composites were compression molded into disks for 5 minutes at a temperature of 200°C and at a pressure of 24 MPa in an electrically heated compression molding press (Carver 4122). The molded samples were cooled in water bath and used further for rheological measurements.

4.2.4 Characterization

The rheological measurements were performed using a Rheometric Scientific ARES N2 dynamic mechanical spectrometer with parallel plate geometry. Tests were
carried out in a strain controlled dynamic frequency mode at 200°C. The rheological properties were determined as a function of frequency from 0.03 to 100 s⁻¹. The strain amplitude was kept constant at 4%.

Tensile measurements were performed according ASTM D 638-00 (type I) at room temperature on an Instron testing machine, Model 5567. The tests were carried out at a crosshead speed of 50 mm/min with a 30 kN load cell. All the results were the average of five measurements.

The unnotched Izod pendulum impact resistance was obtained by using injection molded standard bars with a notch according to ASTM D 256-00. The samples were hit from the backside of the notch. Five specimens were used and averaged results and error range were obtained. 22.241 N (5 lbs) pendulum was used. All tests were performed at room temperature.

In order to study the morphology of the injection molded samples atomic force microscope (AFM) was used. Studies of samples cryomicrotomed at -80°C were done in air at ambient conditions using Dimension 3000 IIIa AFM (Digital Instruments). The tapping mode was used using Si probes (TAP 300, Nano Metrology Devices) with a spring constant of 40 N.m⁻¹, resonance frequencies 300 kHz, and the tip radius less than 10 nm. The AFM topographic (height) and the elastic (phase) images were simultaneously obtained under tapping conditions on the cryomicrotomed surface of PP/clay nanocomposites. Phase images revealed hard regions in dark (clay inclusions) and soft regions in bright (PP matrix).
Using a Rigaku X-ray machine with wavelength $\lambda=1.54$ Å operated at 40 kV and 150 mA, X-ray diffraction patterns were obtained to determine the mean interlayer spacing of the (001) plane ($d_{001}$) for the organoclays and its nanocomposites with polymers. The scanning range was varied form $2\Theta=1.5^\circ$ to $10^\circ$ with increment of $0.02^\circ$ and fixed time of 5s in reflection mode.

A Mettler Toledo Differential Scanning Calorimeter (DSC 821°) was used to determine melting temperature of the polymer/clay nanocomposites. The instrument was calibrated with indium. The experiments were run twice from 20 to 200 °C at the heating rate of 20°C/min under nitrogen atmosphere. The sample weight was about 5-10 mg.

Thermal gravimetric analysis (TGA) was performed on Mettler Toledo thermal analyzer, model TGA/SDTA 851°, at 20°C/min heating rate, from 50 to 600°C under nitrogen atmosphere. Each time about 15 mg of sample was used.

Oxygen transmission rate (OTR) was measured by Illinois Instruments Oxygen Permeation Analyser, Model 8000, according to ASTM D 3985-95. Compression molded films of 20 mils thick were used. A circle of 10 cm in diameter was cut from a film and placed in the chamber. Nitrogen and oxygen flows were set at 0.31 MPa. Purge level was set at 10 units. Each run was timed for 360 minutes.

4.3 Results and Discussion

4.3.1 Process characteristics

The recorded power consumption is the total power consumption, a part of which is dissipated as heat while a part is utilized to disperse clay filler and promote polymer
intercalation into clay inter gallery spacing. However, it is not possible to determine exactly the proportion of power in these two cases. The only thing that can be recorded is the initial power consumption of the system when the horn works without loading and this loss was subtracted from the recorded values of power consumption to give the values used in Figure 4.1. The increase of flow rate generally leads to an increase of power consumption which is an indication that more energy is being transmitted into the system at higher flow rates. However, specific power consumption is lower at higher flow rate. Clearly, the treatment of pure PP requires higher energy than that of nanocomposites. Among two Cloisites, the one with more concentrated surface modifier (15A) shows higher power consumption, which is in a good agreement with the higher die pressure required to sustain flow, as described below.

Figure 4.2 shows the die entrance pressure as a function of flow rate. It can be seen that the pressure increases with flow rate. This is because the die pressure characterizing the resistance to flow is a function of the average residence time of the polymer in the treatment zone and the residence time is inversely proportional to the melt flow rate\textsuperscript{165}. It is seen that PP/Cloisite 15A nanocomposites show much higher die pressure than that of PP/Cloisite 20A having less concentrated surface modifier. This is in accord with the viscosity of systems as reported below.
Figure 4.1 Power consumption as a function of flow rate at different concentrations of Cloisite 15A (open symbols) and Cloisite 20A (solid symbols).
4.3.2 Rheology

The complex viscosity as a function of frequency of PP containing 2.5, 5.0, 10 wt% Cloisite untreated and treated by ultrasound at different flow rates is shown in Figure 4.3, 4.4, 4.5 accordingly. All the samples exhibit shear thinning at the frequency range accessed in these measurements. Furthermore, the viscosity decreases with decreasing flow rate, which can be attributed to increasing polymer degradation at longer residence time in the treatment zone. Interestingly, PP/Cloisite 15A filled systems show a gradual viscosity drop. In contrast, PP/Cloisite 20A nanocomposites exhibit an almost one step viscosity drop from untreated to treated samples. Comparison of melt viscosity values shows that the viscosity of nanocomposites containing Cloisite 15A subjected to a higher level of modification is higher. This correlates with power consumption and die pressure measurements depicted in Figures 4.1 and 4.2.

4.3.3 Structural effects

The XRD patterns in Figures 4.6, 4.7, 4.8 illustrate the effect of ultrasound on the morphology of 2.5, 5.0, 10 wt% clay/PP nanocomposites prepared at different flow rates. 20 values are indicated in parentheses. Based on these data the inter gallery distance of clays and nanocomposites was calculated using Bragg’s Law\textsuperscript{166}. Less change in the basal spacing of Cloisite 15A based composites has been observed. At the same time, the most significant increase in the inter-gallery distance was observed in PP nanocomposites based on 2.5 wt.% Cloisite 20A. In particular, the basal spacing increased from 2.4 nm for pristine clay to 3.5 nm for intercalated clay in the nanocomposite obtained at 0.25 g/s.
Figure 4.2  Die pressure as a function of flow rate at different concentrations of Cloisite 15A (open symbols) and Cloisite 20A (solid symbols).
Figure 4.3 Complex viscosity as a function of frequency for PP containing 2.5 wt% Cloisite 15A (a) and 20A (b) untreated and treated by ultrasound at different flow rates.
Figure 4.4 Complex viscosity as a function of frequency for PP containing 5.0 wt%

Cloisite 15A (a) and 20A (b) untreated and treated by ultrasound at different flow rates.
Figure 4.5 Complex viscosity as a function of frequency for PP containing 10 wt% Cloisite 15A (a) and 20A (b) untreated and treated by ultrasound at different flow rates.
A significant shift of $d_{001}$ peak suggests the presence of two distinct processes, namely, intercalation and partial exfoliation of the clay in the system.

These data were supported further by TEM analysis, results of which are demonstrated in Figure 4.9. Unintercalated composites exhibit the structure depicted in Figure 4.9a. Individual tactoids of the layered clays are visible as regions of alternating narrow, dark, and light bands within the clay particle. This regular structure was disrupted by power ultrasound, and the polymer has entered into the intergallery spacing wherein individual clay layers are dispersed in the polymer matrix, as can be seen in Figure 4.9b. It suggests that a partial exfoliation occurs under treatment by ultrasound. It should be noted that the length of ultrasound treatment in this particular case was about 20 s. This treatment time for successful intercalation and partial exfoliation is substantially lower (by about two orders of magnitude) than that so far achieved in intercalation of polymer/clay nanocomposites, as reported earlier for a prolonged ultrasonic treatment$^{162-164}$.

AFM images obtained under normal and hard tapping condition show the bulk morphology of PP/clay composites Figure 4.10. The brighter area is corresponded to the PP matrix. The darker stripes are made up of the clay inclusions. The individual clay stacks have elongated shape with aspect ratio about 10:1 (average particle dimensions 4 by 0.4 μm). Clay particles are oriented in the direction parallel to the injection molded surface and dispersed homogeneously in the PP matrix. The obtained data suggest that AFM resolution is not high enough to conclude whether an intercalation or partial exfoliation was achieved.
Figure 4.6 XRD patterns of untreated and ultrasonically treated at different flow rates PP based nanocomposites containing 2.5 wt.% of Cloisite 15A (a) and 20A (b).
Figure 4.7 XRD patterns of untreated and ultrasonically treated at different flow rates PP based nanocomposites containing 5.0 wt.% of Cloisite 15A (a) and 20A (b).
Figure 4.8 XRD patterns of untreated and ultrasonically treated at different flow rates PP based nanocomposites containing 10 wt.% of Cloisite 15A (a) and 20A (b).
Figure 4.9. TEM images of PP nanocomposites containing 2.5 wt.% Cloisite 20A untreated (a) and treated with ultrasound at 0.25 g/s flow rate (b).
4.3.4 Mechanical properties

One would expect substantial improvement in the mechanical properties of intercalated/exfoliated nanocomposites when a high aspect ratio is realized. In fact, the elongation at break and toughness (the area under the stress-strain curve) are significantly increased in ultrasonically treated nanocomposites containing 2.5 and 5.0 wt% of clay and obtained at flow rates of 0.25 and 0.5 g/s, as evident from Figure 4.11 indicating the elongation at break as function of flow rate. Clearly, this increase is achieved at residence times when intercalation and partial exfoliation were observed by XRD and TEM. However, other mechanical properties are not substantially affected by ultrasonic treatment. This is because two competing processes simultaneously take place: intercalation/ exfoliation of clay and polymer matrix degradation under the influence of ultrasound. Table 4.1 shows the mechanical properties of PP/clay nanocomposites for different filler content and treatment conditions.

4.3.5 Thermal properties

Results of thermal gravimetric analyses of neat PP and its nanocomposites are illustrated in Figure 4.8. It is clearly seen that the thermal stability of PP/clay nanocomposite is increased by about 40°C.

Table 4.2 summarizes data obtained from DSC analysis of neat PP and its nanocomposites. Degree of crystallinity was calculated for polypropylene samples using the following formula
Figure 4.10. AFM images at different resolution of PP nanocomposites containing 2.5 wt.% Cloisite 20A untreated (left) and treated with ultrasound at 0.25 g/s flow rate (right).
Figure 4.11. Elongation at break as a function of flow rate for PP and its nanocomposites with Cloisite 15A (a) and 20A (b).
Table 4.1 Mechanical properties of untreated and treated at 10 μm amplitude PP and its clay nanocomposites.

<table>
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<th>Sample</th>
<th>Flow Rate, g/s</th>
<th>Modulus at 5% strain, MPa</th>
<th>Yield stress, MPa</th>
<th>Elongation at break, %</th>
<th>Tensile Strength, MPa</th>
<th>Toughness, MPa</th>
<th>Izod Impact Strength, J/m</th>
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\[ \chi = \frac{\Delta H}{\Delta H_0} \times 100\% , \]

where \( \Delta H \) is a heat flux at melting of a given polymer, \( \Delta H_0 \) is a heat flux at melting of the same but 100% crystalline polymer (for isotactic PP 202 J/g\(^{168}\)). Two runs on each sample were performed to eliminate prethermal history. No significant differences in melting temperature and degree of crystallinity were observed for untreated and treated as well as for neat and filled samples.

4.3.6 Oxygen pemeability

Oxygen transmission rates through thin films made of neat PP and its 2.5 wt% Cloisite 20A nanocomposites are shown in Figure 4.13. As one can see introduction of clay into polymer matrix led to significant (two orders of magnitude) decrease in oxygen permeability. Unexpectedly, ultrasonic treatment caused increase in oxygen transmission rates as compared to untreated sample. This effect can be explained by formation of micro voids during ultrasonic treatment. Those voids could not heal while the samples had been compression molded into films used for testing. Such they might form a passage channel for oxygen to permeate.

4.4 Conclusions

A continuous method to achieve rapid intercalation and partial exfoliation of PP/clay nanocomposite without chemical modification of the matrix was developed. Two
competing processes, namely, intercalation/exfoliation of clay and polymer matrix degradation under the influence of ultrasound have been encountered.

Two clays with different levels of modification were studied. The results indicate that the intercalation under ultrasound treatment is higher for nanocomposites containing clay with lower cation exchange capacity.

Under conditions of melt intercalation the elongation at break and toughness were substantially improved. To obtain enhancement in other mechanical properties further modifications of the technique is needed, such as eliminating the compounding stage with a twin screw extruder and shifting toward a one stage process to minimize polymer matrix degradation.
Figure 4.12 TGA curves for PP and its nanocomposites with Cloisite 20A treated by ultrasound at a feed rate of 0.25g/s.
Table 4.2 Thermal properties of PP and its clay nanocomposites.

<table>
<thead>
<tr>
<th>Composition</th>
<th>T&lt;sub&gt;m&lt;/sub&gt;, °C</th>
<th>ΔH, J/g</th>
<th>χ, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1&lt;sup&gt;st&lt;/sup&gt; run</td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; run</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; run</td>
</tr>
<tr>
<td>Neat PP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Profax 6523</td>
<td>171.7</td>
<td>167.7</td>
<td>72.5</td>
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<td>165.8</td>
<td>88.9</td>
</tr>
<tr>
<td>Treated @ 0.25 g/s</td>
<td>169.0</td>
<td>163.7</td>
<td>84.5</td>
</tr>
<tr>
<td>0.5 g/s</td>
<td>168.9</td>
<td>164.5</td>
<td>82.4</td>
</tr>
<tr>
<td>1.0 g/s</td>
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<td>164.4</td>
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<tr>
<td>2.5 wt % Cloisite 15A in PP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated</td>
<td>169.3</td>
<td>167.32</td>
<td>74.4</td>
</tr>
<tr>
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<td>167.5</td>
<td>162.5</td>
<td>78.3</td>
</tr>
<tr>
<td>0.5 g/s</td>
<td>168.3</td>
<td>164.9</td>
<td>80.5</td>
</tr>
<tr>
<td>0.75 g/s</td>
<td>168.3</td>
<td>163.9</td>
<td>82.0</td>
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<tr>
<td>5.0 wt % Cloisite 15A in PP</td>
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<td></td>
<td></td>
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<tr>
<td>Untreated</td>
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<td>165.8</td>
<td>74.7</td>
</tr>
<tr>
<td>Treated @ 0.25 g/s</td>
<td>167.0</td>
<td>162.7</td>
<td>80.5</td>
</tr>
<tr>
<td>0.5 g/s</td>
<td>167.7</td>
<td>162.3</td>
<td>79.4</td>
</tr>
<tr>
<td>0.75 g/s</td>
<td>167.0</td>
<td>162.4</td>
<td>82.0</td>
</tr>
<tr>
<td>10.0 wt % Cloisite 15A in PP</td>
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<tr>
<td>Untreated</td>
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<td>165.6</td>
<td>78.9</td>
</tr>
<tr>
<td>Treated @ 0.25 g/s</td>
<td>166.3</td>
<td>163.7</td>
<td>85.7</td>
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<tr>
<td>0.5 g/s</td>
<td>167.9</td>
<td>164.0</td>
<td>81.2</td>
</tr>
<tr>
<td>0.75 g/s</td>
<td>166.6</td>
<td>162.0</td>
<td>80.6</td>
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</tbody>
</table>
Figure 4.13 Oxygen transmission rate as a function of time for PP and its 2.5 wt% Cloisite 20A nanocomposites untreated and treated by ultrasound at different feed rates.
CHAPTER V
ULTRASOUND AIDED SINGLE STAGE VS TWO STAGE EXTRUSION PROCESS
FOR PREPARATION OF POLYPROPYLENE-CLAY NANOCOMPOSITES

5.1 Introduction

The most recent attempts to develop polymer/clay nanocomposites via melt intercalation in an intensive batch mixer\textsuperscript{162, 163} and a stationary cup\textsuperscript{164} equipped with power ultrasound were reported. However, a prolonged ultrasonic treatment (10-20 mins) was used in these studies, apparently leading to a substantial degradation of polymer matrix. A continuous method to achieve rapid intercalation (7-21 seconds) and partial exfoliation of PP/clay nanocomposite without chemical modification of the matrix was developed\textsuperscript{167}.

In the previous chapter, the two stage ultrasound aided extrusion process was utilized to fabricate PP/clay nanocomposites. It was found that there is a need to minimize polymer matrix degradation by combining compounding and ultrasonic treatment in a single stage. Accordingly, the present study describes a single stage process where the modified screw with mixing elements and an ultrasonic die attachment were used. Two regimes of feeding were realized, namely, starved and flood feeding. The gap size in the ultrasonic treatment zone was varied. Die pressure and power consumption
were measured. The obtained nanocomposites are characterized based on their rheological, mechanical properties, and morphology.

5.2 Experimental

5.2.1 Preparation of blends

The nanocomposites were compounded by a single screw extruder, where the original screw (Figure 3.2b) was replaced by the modified screw with mixing elements (Figure 3.3), and ultrasonic die attachment. Processing was performed using temperature settings in 4 zones and die of 180/200/200/200 °C. Two regimes of feeding were applied, namely, starved (screw speed of 100 rpm) and flood feeding (screw speed variable). The ultrasonic treatment was carried out at a frequency of 20 kHz and two horns. Gap size of 2 mm and 4 mm were used in addition to three different flow rates of the material (0.25, 0.5, and 0.75 g/s) to vary residence time. Only Cloisite 20A at the filling level of 2.5 wt.% has been considered since it had shown better interaction with PP matrix.

5.2.2 Molding

The pellets of PP/clay materials were injection molded in a Van Dorn 55 injection molding machine. The process parameters were listed in Table 3.2.

The obtained PP/clay composites were compression molded into disks for 5 minutes at a temperature of 200°C and at a pressure of 24 MPa in an electrically heated
compression molding press (Carver 4122). The molded samples were cooled in water bath and used further for rheological measurements.

5.2.3 Characterization

The rheological measurements were performed using a Rheometric Scientific ARES N2 dynamic mechanical spectrometer with parallel plate geometry. Tests were carried out in a strain controlled dynamic frequency mode at 200°C. The rheological properties were determined as a function of frequency from 0.03 to 100 s⁻¹. The strain amplitude was kept constant at 4%.

Tensile measurements were performed according ASTM D 638-00 (type I) at room temperature on an Instron testing machine, Model 5567. The tests were carried out at a crosshead speed of 50 mm/min with a 30 kN load cell without an extensometer. All the results were the average of five measurements.

The unnotched Izod pendulum impact resistance was obtained by using injection molded standard bars with a notch according to ASTM D 256-00. The samples were hit from the backside of the notch. Five specimens were used and averaged results and error range were obtained. 22.241 N (5 lbs) pendulum was used. All tests were performed at room temperature.

In order to study the morphology of the nanocomposites a Rigaku X-ray machine with wavelength $\lambda=1.54$ Å operated at 40 kV and 150 mA was used to determine the mean interlayer spacing of the (001) plane ($d_{001}$) for the organoclays and its
nanocomposites with polymers. The scanning range was varied form $2\Theta=1.5^\circ$ to $10^\circ$ with increment of $0.02^\circ$ and fixed time of 5 s in reflection mode.

5.3 Results and Discussion

5.3.1 Process characteristics

Figure 5.1 shows the power consumption of ultrasonically treated PP/C20A composites obtained at different feeding regimes and variable gap size. An increase of flow rate leads to an increase in power consumption which is an indication that more energy is being transmitted into the system at higher flow rates. Clearly, the treatment of pure PP requires higher energy than that of nanocomposites at the gap size of 4 mm. With a reduction in the gap size the power consumption increases due to the increase in the strain amplitude imposed on the polymer melt.

Figure 5.2 shows the die entrance pressure as a function of flow rate. It can be seen that the pressure increases with flow rate. This is because the die pressure characterizing the resistance to flow is a function of the average residence time of the polymer in the treatment zone and the residence time is inversely proportional to the melt flow rate\textsuperscript{165}. Therefore, due to the longer residence time the effect of ultrasound in a larger gap should be expected to be greater. However, for a larger gap at the same amplitude, the strain amplitude determining the effect of ultrasound on polymers is lower. Evidently, due to the increase of the strain amplitude, the effect of ultrasonic amplitude on the reduction of the melt viscosity is much stronger at smaller gaps than at
Figure 5.1 Power consumption as a function of flow rate for neat PP and PP/Cloisite 20A nanocomposites obtained by single stage (starved or flood fed) and two stage processes.
Figure 5.2 Die pressure as a function of flow rate for neat PP and PP/Cloisite 20A nanocomposites obtained by single stage (starved or flood fed) and two stage processes.
larger gaps, even though the residence time is shorter in smaller gaps. This is in accord with the viscosity of systems as reported below.

5.3.2 Rheology

The complex viscosity behavior of PP containing 2.5 wt% Cloisite 20A untreated and treated by ultrasound at different flow rates is shown in Figure 5.3. All the samples exhibit shear thinning at the frequency range accessed in these measurements. Furthermore, the viscosity decreases with decreasing flow rate, which can be attributed to increasing polymer degradation at longer residence times in the treatment zone. Nanocomposites prepared using single stage process exhibit higher viscosity values in the measured range as evident from comparison of Figure 5.3a and Figure 5.3 b. This supports the expectation of less polymer degradation while switching from the two to the single stage process. However, a decrease in the gap size leads to a significant drop in viscosity compared to that of the two stage process.

5.3.3 Morphology

The XRD patterns in Figure 5.4 illustrate the effect of ultrasound on morphology of 2.5 wt% clay/PP nanocomposites prepared at various flow rates. Based on this data the inter gallery distance of clays and nanocomposites was calculated using Bragg’s Law. Less change in the basal spacing of Cloisite 20A based composites has been observed at single stage process, starved feeding, and 4 mm gap. At the same time, the most
Figure 5.3 Complex viscosity as a function of frequency for PP containing 2.5 wt% Cloisite 20A obtained by two stage process (a); single stage starved feeding (b), flood feeding process with gap size of 4mm (c) and 2mm (d) untreated and treated by ultrasound at different flow rates.
Figure 5.4 XRD patterns of untreated and ultrasonically treated at different flow rates PP based nanocomposites containing 2.5 wt.% of Cloisite 20A obtained by two stage process (a); single stage starved feeding (b), flood feeding process with gap size of 4mm (c) and 2mm (d). 2θ values are indicated in parentheses.
significant increase in the inter-gallery distance was observed in nanocomposites obtained by single stage, flood feeding, 2 mm gap, and flow rate of 0.25 g/s.

In particular, the basal spacing increased from 2.4 nm for pristine clay to 4.1 nm for intercalated clay in the nanocomposite obtained at the mentioned conditions. A significant decrease in intensity of $d_{001}$ peak suggests the presence of two distinct processes, namely, intercalation and partial exfoliation of the clay in the system. It should be noted that the length of ultrasound treatment in this particular case was 21 seconds. This treatment time for successful intercalation and partial exfoliation is substantially lower (by about two orders of magnitude) than that so far achieved in intercalation of polymer/clay nanocomposites reported earlier for a prolonged ultrasonic treatment\textsuperscript{162-164}.

5.3.4 Mechanical properties

The elongation at break and toughness (the area under the stress-strain curve) are significantly increased in ultrasonically treated nanocomposites containing 2.5 wt% of clay and obtained at flow rates of 0.25 and 0.5 g/s with two stage and flood fed single stage processes (2 mm gap), as evident from Figure 5.5 indicating the elongation at break as a function of flow rate. Clearly, this increase is achieved at residence times when intercalation and partial exfoliation were observed by XRD. Other mechanical properties are not substantially affected by ultrasonic treatment as indicated by data in Table 5.1. This is because two competing processes simultaneously take place: intercalation/exfoliation of clay and polymer matrix degradation under the influence of ultrasound.
Figure 5.5 Elongation at break as a function of flow rate for rate for neat PP and PP/Cloisite 20A nanocomposites obtained by single stage (starved or flood fed) and two stage processes.
Table 5.1 Mechanical properties of neat PP and its Cloisite 20A nanocomposites obtained at different ultrasonic treatment conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cloisite 20A c, wt%</th>
<th>Gap size mm</th>
<th>Flow rate, g/s</th>
<th>Modulus MPa</th>
<th>Yield stress MPa</th>
<th>Elongation at break %</th>
<th>Tensile Strength MPa</th>
<th>Toughness MPa</th>
<th>Izod Impact Strength, J/m</th>
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<tbody>
<tr>
<td>0 (neat PP) starved fed</td>
<td>4</td>
<td>untreated</td>
<td>553</td>
<td>34.6</td>
<td>73.9</td>
<td>19.4</td>
<td>19</td>
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<td></td>
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<tr>
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<td></td>
<td></td>
<td>0.25</td>
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<td>456</td>
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<td>15.3</td>
<td>49</td>
<td>578</td>
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<td>267.0</td>
<td>14.9</td>
<td>50</td>
<td>393</td>
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<tr>
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<td>28.8</td>
<td>704</td>
<td>24.0</td>
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</table>
5.4 Conclusions

Two methods for the fabrication of PP/clay nanocomposites using a continuous ultrasound assisted process were compared. Two competing processes, namely, intercalation/ exfoliation of clay and polymer matrix degradation under the influence of ultrasound have been encountered. Single stage process led to less polymer degradation at the fixed gap size.

Variations of feeding regimes and gap size during single stage process were studied. Results indicate that intercalation under ultrasound was higher for flood feeding and for smaller gap. Polymer matrix degradation was substantial at the same conditions.

The elongation at break and toughness were substantially improved for nanocomposites produced by the single stage process. However, this improvement did not exceed that of the materials derived by the two stage process. To obtain enhancement in other mechanical properties further investigation of the processing conditions is needed, such as increasing processing temperature and increasing die pressure to aid the filler dispersion.
CHAPTER VI

EVALUATION EFFECT OF MALEIC ANHYDRIDE AS COMPATIBILIZER FOR POLYPROPYLENE-CLAY HYBRIDS IN COUPLING WITH POWER ULTRASOUND

6.1 Introduction

Polypropylene is one of the fastest growing classes of thermoplastics. This growth is attributed to its attractive combination of low cost, low density, and high heat distortion temperature. The extraordinary versatility of unfilled virgin resin and reinforced polypropylene suits a wide spectrum of end-use applications for fiber, films, and molded parts. However, there always exist certain shortcomings in physical and chemical properties that can limit universal use of any given polymer resin. In packaging, for example, polypropylene resins have poor oxygen barriers, while low dimensional and thermal stability limits the scope of polypropylene composites in automotive applications. One of the schemes to improve the above properties involves filling of polypropylene matrix with organically modified montmorillonite. The main challenge in preparation of such composites is that polypropylene being too much apolar to correctly interact with the
modified layers \textsuperscript{62}. One the techniques used to overcome this problem is functionalization of the polypropylene chain by maleic anhydride (MA) \textsuperscript{25,26,67,169-174}.

With this in mind, the present study describes the effect of maleic anhydride modification in coupling with the ultrasonic treatment on controlling the structure and properties of PP-MA/clay nanocomposites. Rheological properties, morphology, and mechanical properties of the untreated and ultrasonically treated nanocomposites were investigated.

6.2 Experimental

6.2.1 Preparation of hybrids

The nanocomposites were compounded by a single screw extruder, where the original screw (Figure 3.2b) was replaced by the modified screw with mixing elements (Figure 3.3), and ultrasonic die attachment. Processing was performed using temperature settings in 4 zones and die of 180/200/200/200 \degree\text{C}. The ultrasonic treatment was carried out at a frequency of 20 kHz and two horns. Gap size of 4 mm was used. Feed rate was 0.75 g/s. Polybond 3002 content was kept constant at 10 wt\%. Only Cloisite 20A at the filling level of 5 wt \% has been considered since it had shown better interaction with PP matrix. Here and further the composition PP/PP-MA/Clay 85/10/5 wt\% is designated as MPPC (maleinated PP/Clay nanocomposite).
6.2.2 Molding

The pellets of MPPC materials were injection molded in a Van Dorn 55 injection molding machine. The process parameters were listed in Table 3.2.

The obtained MPPC were compression molded into disks for 5 minutes at a temperature of 200°C and at a pressure of 24 MPa in an electrically heated compression molding press (Carver 4122). The molded samples were cooled in water bath and used further for rheological measurements.

6.2.3 Characterization

The rheological measurements were performed using a Rheometric Scientific ARES N2 dynamic mechanical spectrometer with parallel plate geometry. Tests were carried out in a strain controlled dynamic frequency mode at 200°C. The rheological properties were determined as a function of frequency from 0.03 to 100 s⁻¹. The strain amplitude was kept constant at 4%.

Tensile measurements were performed according ASTM D 638-00 (type I) at room temperature on an Instron testing machine, Model 5567. The tests were carried out at a crosshead speed of 50 mm/min with a 30 kN load cell. All the results were the average of five measurements.

The unnotched Izod pendulum impact resistance was obtained by using injection molded standard bars with a notch according to ASTM D 256-00. The samples were hit from the backside of the notch. Five specimens were used and averaged results and error
range were obtained. 22.241 N (5 lbs) pendulum was used. All tests were performed at room temperature.

In order to study the morphology of the nanocomposites a Rigaku X-ray machine with wavelength $\lambda=1.54$ Å operated at 40 kV and 150 mA was used to determine the mean interlayer spacing of the (001) plane ($d_{001}$) for the organoclays and its nanocomposites with polymers. The scanning range was varied form $2\Theta=1.5^\circ$ to $10^\circ$ with increment of $0.02^\circ$ and fixed time of 5 s in a reflection mode.

6.3 Results and Discussion

6.3.1 Process characteristics

The power consumption measured is the total energy used during the treatment. The power consumption of horns working without load, zero power consumption, was subtracted from the total power consumption. Power consumption increased with modification of PP and introduction of filler (Figure 6.1). This indicated that more energy was transmitted from horns into the polymer melt.

Figure 6.2 shows die pressure at the entrance to ultrasonic treatment zone during ultrasonic treatment of PP/PPMA based nanocomposites. Pressure at the treatment zone was substantially reduced as the ultrasound was applied. Ultrasound induces degradation of polymer and facilitates the flow of melt. It is seen that MPPC nanocomposites show higher die pressure than that of unfilled PP. This is in accord with the viscosity of systems as reported below.
Figure 6.1 Power consumption during ultrasonic treatment of neat PP, PP modified by MA and MPPC obtained at 0.75 g/s feed rate.
Figure 6.2  Die pressure as a function of flow rate for neat PP, PP modified by MA and MPPC nanocomposite untreated and treated by ultrasound at 0.75 g/s feed rate.
6.3.2 Rheology

The complex viscosity as a function of frequency of neat PP, PP modified by MA and MPPC nanocomposite untreated and treated by ultrasound at 0.75 g/s feed rate is shown in Figure 6.3. The samples exhibit shear thinning at the frequency range accessed in these measurements. Furthermore, the viscosity decreases with application of ultrasound, which can be attributed to increasing polymer degradation.

Modification of PP by maleic anhydride led to slight, but expected decrease in viscosity due to low molecular weight (high MFI) of Polybond 3002. On the other hand, one would expect an increase in viscosity of modified PP, mainly, due to grafting. But this effect was evidently overcome by “dilution” of the system.

The melt viscosity of hybrid polymer nanocomposites is related to the aspect ratio of individual platelets. The aspect ratio of the platelet is then related to the intercalation of the clay. Therefore, the aspect ratio is changing according to different levels of intercalation. It can be seen, that filling of PP/PPMA with 5wt% of clay leads to viscosity increase. Treatment by ultrasound induces polymer matrix degradation and as a result viscosity drops. Since the breakage of the C-C bond by ultrasound usually follows free radical mechanism, maleic anhydride can accelerate this process due to the presence of rather reactive C-O and C=O bonds.
Figure 6.3 Complex viscosity as a function of frequency for neat PP, PP modified by MA and MPPC nanocomposite untreated and treated by ultrasound at 0.75 g/s feed rate.
6.3.3 Morphology

The XRD patterns in Figure 6.4 illustrate the effect of ultrasound on the morphology of untreated and ultrasonically treated at 0.75 g/s feed rate PP-MA based nanocomposites containing 5.0 wt.% of Cloisite 20A. Based on these data the inter gallery distance of clays and nanocomposites was calculated using Bragg’s Law\textsuperscript{166}. The basal spacing increased from 2.4 nm for pristine clay to 3.0 nm for intercalated clay in the nanocomposite obtained by simple melt mixing. Further ultrasonic treatment led to decrease of interlayer spacing to 2.7 nm. Based on this comparison, in binary mixtures of PP/org-MMT it is speculated that state of dispersion can be improved under sufficient level of imposed stress provided that the org-MMT renders an appropriate entropic contribution. However, the excessive stress may induce compression or other types of similar actions on the surface of the layered silicates, leading to decrease in d-spacing of org-MMT \textsuperscript{174}. Therefore, it is fair to suggest that ultrasound played a compacting role rather than dispersing at the specified degree of filling.

6.3.4 Mechanical properties

Mechanical properties of PP modified by MA and its 5 wt% clay nanocomposite untreated and treated by ultrasound at 0.75 g/s feed rate are summarized in Table 6.1. As one can see all mechanical properties remained unchanged or worsen as a result of ultrasonic treatment in this particular case. It can be explained by the fact that polymer matrix degradation prevailed all other positive effects of ultrasound such as aid in intercalation and exfoliation of clay platelets into polymer.
Figure 6.4 XRD patterns of Cloisite 20A, untreated and ultrasonically treated MPPC nanocomposites at 0.75 g/s feed rate. 2θ values are indicated in parentheses.
Trends common for microcomposites have been observed. First of all, Young’s modulus increases with addition of filler to polymeric matrix, which is considered to be a reinforcing effect. Secondly, Izod impact strength drops due to filler particles being stress concentrators.

6.4 Conclusions

Ultrasonic treatment improved the processing behavior of PP/PPMA based nanocomposites by reducing the die pressure. Ultrasound power consumption increased with modification of PP and introduction of filler.

MPPC hybrids underwent degradation during ultrasonic treatment. The degradation of polymeric matrix was accelerated by the presence of maleic anhydride.

The opposite effect to expected dispersion with aid of ultrasound has been encountered. Namely, collapse of intercalated structures under ultrasonic treatment was observed.

Mechanical properties of MPPC nanocomposite untreated and treated by ultrasound were not improved.

Therefore, no synergetic effect between polypropylene modification with maleic anhydride and treatment by high power ultrasound in preparation of polymer based nanocomposites has been detected.
Table 6.1 Mechanical properties of PP modified by MA and MPPC nanocomposite untreated and treated by ultrasound at 0.75 g/s feed rate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flow Rate, g/s</th>
<th>Modulus at 5% strain, MPa</th>
<th>Yield stress, MPa</th>
<th>Elongation at break, %</th>
<th>Tensile Strength, MPa</th>
<th>Toughness, MPa</th>
<th>Izod Impact Strength, J/m</th>
</tr>
</thead>
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<td>0/10.5/89.5</td>
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<td>96.5</td>
<td>13.0</td>
<td>21.1</td>
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<td>10.6</td>
<td>28.5</td>
<td>1228</td>
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<tr>
<td>5/10/85</td>
<td>untreated 0.75</td>
<td>694</td>
<td>29.3</td>
<td>111</td>
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<td>21.7</td>
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<tr>
<td></td>
<td></td>
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<td>28.3</td>
<td>82.9</td>
<td>12.8</td>
<td>17.4</td>
<td>379</td>
</tr>
</tbody>
</table>
CHAPTER VII

ULTRASONIC ASSITED EXTRUSION OF HDPE/CLAY NANOCOMPOSITES

7.1 Introduction

Polymer nanocomposites have opened a new horizon for a promising class of hybrid materials by incorporation of particulate fillers into polymer matrices to improve or modify properties of neat polymers. In recent years, layer-silicate based polymer nanocomposites have attracted considerable technological and scientific interest for their changes in thermal\textsuperscript{175}, rheological\textsuperscript{176}, mechanical\textsuperscript{177} and physical\textsuperscript{178} properties of polymers. In general, the layer silicate is modified with alkylammonium, which is hydrophilic and this facilitates its interaction with the polymer. When a thermoplastic polymer is mixed with an organoclay, it either intercalates or exfoliates the layer silicate aggregates. In general, the intercalation is obtained when polymer matrix and layer silicates do not have sufficient attractive interactions, while exfoliation is observed when they have strong attractive interactions. Polyethylene is one of the most widely used polymers which do not have any polar groups in its backbone, to interact with clay surface for dispersion. However, by incorporating a compatibilizer into the system, it is possible to improve dispersion of clay with polymer matrix\textsuperscript{179}. Although the methods have proved to be capable of nanocomposites formation, the exfoliation of the clays
silicate layers is incomplete and thus, the reinforcement effect is limited especially for the polyolefins like HDPE. Despite of the considerable number of studies concerned with the preparation, characterization and properties of polyethylene/clay nanocomposites, no report has been published regarding the processing of HDPE/clay nanocomposites by continuous ultrasonic assisted extrusion process. It was observed that long-chain polymer molecules can be ruptured by high intensity ultrasound during melt extrusion\(^{180}\) leading to the formation of long chain radicals. In polymer clay systems, polymeric radicals may combine with the surface modifying agent of the clay forming a chemical bond. Another important aspect of the ultrasound assisted process was to facilitate break up and delamination layer silicate, which is essential for the nanoscale dispersion of clays during melt mixing with the polymer matrix in batch mixer\(^{181}\) and extruder\(^{187}\). The present study describes the effect of continuous supply of ultrasonic energy of varying amplitude during the melt intercalation of HDPE/clay nanocomposites.

7.2 Experimental

7.2.1 Preparation of hybrids

High density polyethylene (HDPE) was HNM 4550-03-Marlex (Phillips) and was used as received. Cloisite\textsuperscript{®} 20A natural montmorillonite, modified with quaternary ammonium salt (dimethyl, hydrogenated tallow, quaternary ammonium chloride), with a cation exchange capacity of 95 meq/100g and d-spacing of 2.42 nm was supplied by Southern Clay Product, Inc. HDPE/clay nanocomposites with varying clay content of 2.5, 5.0 and 10.0 wt% were prepared by a single screw compounding extruder with Maddock
followed by Melt Star mixing sections and the ultrasonic die attachment. Ultrasound at a frequency of 20 KHz and amplitudes of 5µm, 7.5 µm and 10 µm was used. The screw speed was set at 100 rpm and temperatures were 180 °C, 190 °C and 200 °C from the feeding section to the die zones, respectively. The gap in the slit die was 4 mm. The material was ultrasonically treated in the molten state at three different flow rates of 0.25 g/s, 0.50 g/s and 0.75 g/s, corresponding to the residence time in the treatment zone of 21 s, 10 s and 7 s, respectively.

7.2.2 Molding

The pellets of HDPE/clay materials were injection molded in a Van Dorn 55 injection molding machine. The process parameters were listed in Table 3.2.

The obtained HDPE/clay composites were compression molded into disks for 5 minutes at a temperature of 200°C and at a pressure of 24 MPa in an electrically heated compression molding press (Carver 4122). The molded samples were cooled in water bath and used further for rheological measurements.

7.2.3 Characterization

The rheological measurements were performed using a Rheometric Scientific ARES N2 dynamic mechanical spectrometer with parallel plate geometry. Tests were carried out in a strain controlled dynamic frequency mode at 200°C. The rheological
properties were determined as a function of frequency from 0.03 to 100 s⁻¹. The strain amplitude was kept constant at 4%.

Tensile measurements were performed according ASTM D 638-00 (type I) at room temperature on an Instron testing machine, Model 5567. The tests were carried out at a crosshead speed of 50 mm/min with a 30 kN load cell. All the results were the average of five measurements.

The unnotched Izod pendulum impact resistance was obtained by using injection molded standard bars with a notch according to ASTM D 256-00. The samples were hit from the backside of the notch. Five specimens were used and averaged results and error range were obtained. 22.241 N (5 lbs) pendulum was used. All tests were performed at room temperature.

In order to study the morphology of the nanocomposites a Rigaku X-ray machine with wavelength λ=1.54 Å operated at 40 kV and 150 mA was used to determine the mean interlayer spacing of the (001) plane (d₀₀₁) for the organoclays and its nanocomposites with polymers. The scanning range was varied form 2Θ=1.5° to 10° with increment of 0.02° and fixed time of 5s in a reflection mode.

Oxygen transmission rate (OTR) was measured by Illinois Instruments Oxygen Permeation Analyzer, Model 8000, according to ASTM D 3985-95. Compression molded films of 20 mils thick were used.
7.3 Results and Discussion

7.3.1 Process characteristics

The die pressure of the single screw extruder and the power consumption due to ultrasonic treatment were recorded. It was observed that the die pressure increases with increase of flow rate of HDPE/clay nanocomposites at all concentrations of clay and amplitude of ultrasound (Figure 7.1a). This is because the die pressure characterizing the resistance to flow with clay loading is function of the average residence time of the polymer/clay in the treatment zone and the residence time is inversely proportional to the melt flow rate and directly proportional to the die gap\textsuperscript{165}.

It was also observed that the die pressure decreases substantially with the application of ultrasound of increasing amplitude (Figure 7.1b). This may be due to reduction in friction between the HDPE/clay melt and the die walls due to ultrasonic vibration\textsuperscript{182}. It was found in all sets of experiments, the die pressure of neat polymer is always more than that of the polymer/clay nanocomposites.

The power consumption due to ultrasound treatment is the total power consumption, a part of which is dissipated as heat while a part is utilized to disperse clay filler and promote polymer intercalation into clay gallery. Figure 7.2 shows the power consumption as a function of feeding rates for different concentrations of clay. It was found that, power consumption increasing with increase of feeding rate for all clay concentrations. As a result, more energy is being transmitted into the system at higher feeding rate. It was also observed that the treatment of pure HDPE required higher energy than that of the HDPE/clay nanocomposites.
Figure 7.1 Die pressure as a function of flow rate at fixed amplitude (a) and as a function of amplitude (b) at fixed feeding rate for different concentrations of clay in HDPE.
Figure 7.2 Power consumption as a function of flow rate at different concentrations of clay in HDPE.
7.3.2 Rheology

The complex viscosity of nanocomposites as a function of frequency at different clay content and ultrasonic amplitudes is illustrated in Figure 7.3. It was found that complex viscosity of nanocomposites increases with increase of clay concentration. Complex viscosity of nanocomposites further increased with ultrasonic treatment and attained its maximum level at 5μm amplitude. Complex viscosity decreased at higher amplitudes. Similar trends have been obtained for all concentrations of clay. The increase of complex viscosities of ultrasonically treated nanocomposites was attributed to the nanoscale dispersion of clay within HDPE as a result of improved compatibility between polymer matrix and layered silicate. The results of storage moduli at different amplitudes of ultrasound and results of loss moduli at different concentrations of clay are shown in Figures 7.5 and 7.6, respectively. Storage (G') and loss (G'') moduli increased with increase of clay concentration. After treatment by ultrasound these properties increased further at 5 μm but decreased at higher amplitude of ultrasound. At low frequencies, G' and G'' functions were widely separated, while they were slightly separated at high frequency region. After ultrasonic treatment, a sudden increase of G' was observed at 5 μm amplitude and it slowly decreased at higher amplitudes. This was attributed to the improved compatibilization effect of ultrasound in HDPE/clay nanocomposites.

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Figure 7.3 Complex viscosity as a function of frequency for HDPE and its clay nanocomposites.
Figure 7.4 Storage (a) and loss moduli (b) as a function of frequency for HDPE and its clay nanocomposites.
Figure 7.5 Storage (a) and loss (b) moduli as a function of frequency of HDPE containing 10 wt% of clay ultrasonically treated at different amplitudes.
Figure 7.6 Storage (a) and loss (b) moduli as a function of frequency of untreated HDPE-clay composites with various clay content.
7.3.3 Structural Effects

The XRD patterns in Figure 7.6 illustrate the effect of ultrasound on morphology of 2.5 wt% clay/HDPE nanocomposites prepared at varying flow rates. Based on this data the inter gallery distance of clays and nanocomposites was calculated using Bragg’s Law\textsuperscript{166}. The most significant increase in the inter-gallery distance was observed in nanocomposites obtained at flow rate of 0.25 g/s.

In particular, the basal spacing increased from 2.4 nm for pristine clay to 3.8 nm for intercalated clay in the HDPE/clay nanocomposite obtained at 0.25 g/s flow rate. A significant decrease in intensity of \(d_{001}\) peak suggests the presence of two distinct processes, namely, intercalation and partial exfoliation of the clay in the system.

These data were supported further by TEM analysis, results of which are demonstrated in Figure 7.7. Unintercalated composites exhibit the structure depicted in Figure 7.7a. Individual tactoids of the layered clays are visible as regions of alternating narrow dark and light bands within the nanocomposite. This regular structure was disrupted by power ultrasound, and the polymer has entered into the inter gallery spacing wherein individual clay layers are dispersed in the polymer matrix, as can be seen in Figure 7.7b. It suggests that a partial exfoliation occurs under treatment by ultrasound.

It should be noted that the length of ultrasound treatment in this particular case was 21 seconds. This treatment time for successful intercalation and partial exfoliation is substantially lower (by about two orders of magnitude) than that so far achieved in
Figure 7.7 XRD patterns of untreated and ultrasonically treated at different flow rates HDPE based nanocomposites containing 2.5 wt.% of Cloisite 20A. $\theta$ values are indicated in parentheses.
Figure 7.8 TEM images of HDPE nanocomposites containing 2.5 wt.% Cloisite 20A untreated (a) and treated with ultrasound at 0.25 g/s flow rate (b).
intercalation of polymer/clay nanocomposites reported earlier for a prolonged ultrasonic treatment$^{162-164}$.

7.3.4 Crystallinity Behavior

DSC melting and crystallization curve of the HDPE, untreated HDPE/clay and ultrasonically treated nanocomposites were obtained. Results are summarized in Table 7.1. The degree of crystallinity ($\chi$) of nanocomposites was determined by the equation:

$$\chi = \frac{\Delta H}{\Delta H_0} \times 100\%,$$

where $\Delta H$ is a heat flux at melting of a given polymer, $\Delta H_0$ is a heat flux at melting of the same but 100% crystalline polymer (for HDPE 292 J/g$^{183}$). Results showed that, the degree of crystallinity of nanocomposites tends to decrease slightly with increase of clay contents. At the same time crystallinity decreased considerably at the ultrasound amplitude of 5 μm and increased at higher amplitudes. It happened due to the creation of higher interfacial area between the polymer matrix and the clay, which acts to reduce the mobility of polymer chains. Similar trends have also been reported to occur in polyethylene/vermiculite nanocomposites$^{184}$. Apparently, the interaction of polymer matrix and clay may be reduced by increasing amplitude of ultrasound, and thus increasing crystallinity.
Table 7.1. Degree of crystallinity of HDPE/clay nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>c, %</th>
<th>Amplitude, μm</th>
<th>$\Delta H$, J/g</th>
<th>$\chi$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>179.5</td>
<td>61.5</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>0</td>
<td>173.9</td>
<td>61.1</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>0</td>
<td>165.5</td>
<td>59.7</td>
</tr>
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<td>4</td>
<td>10</td>
<td>0</td>
<td>153.8</td>
<td>58.5</td>
</tr>
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<td>5</td>
<td>5</td>
<td>118.1</td>
<td>40.4</td>
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<td>6</td>
<td>5</td>
<td>7.5</td>
<td>159.9</td>
<td>54.8</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>10</td>
<td>163.7</td>
<td>56.1</td>
</tr>
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</table>
7.3.5 Mechanical properties

The mechanical properties, including yield stress and yield strain, elongation at break of all the nanocomposites prepared in this study, together with the corresponding values of the virgin polymer have been plotted in Figures 7.9 and 7.10. Other mechanical properties were summarized in Table 7.2. The Young’s modulus of nanocomposites increased significantly with the increase of clay loading and decreased slightly with increasing ultrasound amplitude. The yield stress (Figure 7.9a) of ultrasonically treated nanocomposites was more than that of the untreated samples. The yield strain (Figure 7.9b) of untreated nanocomposites decreased monotonically with increase of clay concentration except 10 wt.%. Due to their rigidity, clay filler particles cannot be deformed by external stress in the specimen but act only as stress concentrators during deformation process\textsuperscript{185}. The elongation at break (Figure 7.10) of nanocomposites decreased tremendously with increasing clay content. The elongation at break increased more than two times for ultrasonically treated nanocomposites compared to the untreated samples. Therefore, ultrasound played a vital role in dispersion of clay in HDPE, creating a strong interfacial adhesion with the matrix and the increases extensibility during tensile deformation.

7.3.6 Oxygen permeability

Results of oxygen transmission rate (OTR) through thin films made of HDPE and its clay hybrids are shown in Figures 7.11 and 7.12. It is clearly seen that OTR does not change with introduction of 2.5 wt% clay to the polyethylene matrix. When ultrasound
Figure 7.9 Yield stress (a) and yield strain (b) as a function of ultrasonic amplitude at different clay concentrations.
Figure 7.10 Elongation at break as a function of ultrasonic amplitude at different clay concentrations.
Table 7.2 Mechanical properties of HDPE/clay nanocomposites

<table>
<thead>
<tr>
<th>Sample, (%/μm)</th>
<th>Young’s Modulus, MPa</th>
<th>Elongation at Break, %</th>
<th>Toughness, (MPa)</th>
<th>Yield Strain (%)</th>
<th>Yield Stress (MPa)</th>
<th>Izod Impact Strength, J/m</th>
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<td>908</td>
<td>142.7</td>
<td>24.8</td>
<td>18.1</td>
<td>837</td>
</tr>
<tr>
<td>2.5 / 0</td>
<td>324</td>
<td>679</td>
<td>82.4</td>
<td>24.6</td>
<td>18.1</td>
<td>932</td>
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<td>459</td>
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<td>21.1</td>
<td>18.1</td>
<td>926</td>
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<td>17.4</td>
<td>288</td>
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<td>19.0</td>
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<td>942</td>
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<tr>
<td>5 / 10</td>
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<td>835</td>
<td>109.5</td>
<td>19.1</td>
<td>19.8</td>
<td>893</td>
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</table>
was applied to treat HDPE/clay melt, a significant decrease of OTR by 20% was observed. OTR data for different clay contents and various processing conditions are summarized in Table 7.3. The best barrier properties have been achieved for 2.5 wt% clay / HDPE nanocomposite obtained at 0.25 g/s feed rate and 10μm ultrasound amplitude. This occurs at the processing conditions when intercalation and partial exfoliation of clay into polymeric matrix have been reported.

The effect of clay concentration on OTR is illustrated in Figure 7.12. Barrier properties remain unchanged at clay content of 2.5 and 5 wt%, while introduction of 10 wt% of clay leads to increase of OTR. It can be explained by the fact that at higher clay content the system becomes overcrowded and mineral particles turn into defects instead of barrier as expected. Further treatment by ultrasound leads to improvement of barrier properties of HDPE/clay nanocomposites as mentioned before.

7.4 Conclusions

A continuous method to achieve rapid intercalation and partial exfoliation of HDPE/clay nanocomposite without chemical modification of the matrix was developed. The effect of ultrasound amplitude on properties of obtained nanocomposites has been investigated.

Two competing processes, namely, intercalation/ exfoliation of clay and polymer matrix degradation under the influence of ultrasound have been encountered as evident from rheological data indicating highest viscosity data at 5 μm ultrasound amplitude.
Figure 7.11 Oxygen transmission rate as a function of time for HDPE and its 2.5 wt% clay nanocomposites untreated and treated by ultrasound at different feed rates.
Table 7.3 Oxygen transmission rate of HDPE/clay nanocomposites at different clay content and various processing conditions

<table>
<thead>
<tr>
<th>c, wt%</th>
<th>Amplitude, µm</th>
<th>Feed rate, g/s</th>
<th>OTR, cm³/m²/day</th>
</tr>
</thead>
<tbody>
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<td>75.9</td>
</tr>
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<td>0</td>
<td>0.75</td>
<td>76.2</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0.75</td>
<td>76.4</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0.75</td>
<td>79.7</td>
</tr>
<tr>
<td>2.5</td>
<td>5</td>
<td>0.75</td>
<td>76.8</td>
</tr>
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<td>7.5</td>
<td>0.75</td>
<td>80.6</td>
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<td>10</td>
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<tr>
<td>2.5</td>
<td>10</td>
<td>0.25</td>
<td>61.8</td>
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</table>
Figure 7.12 Oxygen transmission rate as a function of time for HDPE and its nanocomposites of various clay contents obtained without and with treatment by ultrasound at different feed rates.
Intercalation and exfoliation of clay into polyethylene have been observed by TEM and supported by XRD measurements.

It was identified that the degree of crystallinity of nanocomposites tends to decrease slightly with increase of clay contents. At the same time crystallinity decreased considerably at the ultrasound amplitude of 5 μm and increased at higher amplitudes.

Under conditions of melt intercalation the elongation at break and toughness were substantially improved. The Young’s modulus of nanocomposites increased significantly with the increase of clay loading and decreased slightly with increasing ultrasound amplitude. The yield stress of ultrasonically treated nanocomposites was more than that of the untreated samples. The yield strain of untreated nanocomposites decreased monotonically with increase of clay concentration and also with ultrasonic amplitude.

Oxygen transmission rate remains unchanged with introduction of low clay content without ultrasonic treatment while ultrasound treatment improved barrier properties by 20%.
CHAPTER VIII

COMPARISON OF POLYPROPYLENE AND POLYETHYLENE CLAY HYBRIDS
PREPARED WITH AID OF POWER ULTRASOUND

8.1 Introduction

Polyethylene and polypropylene are commodity thermoplastics which are widely used due to their attractive combination of low cost, low density, and high heat distortion temperature. The extraordinary versatility of unfilled virgin resins and reinforced matrices suit a wide spectrum of end-use applications for fibers, films, and molded parts. However, there always exist certain shortcomings in physical and chemical properties that limit the use of any given polymer resin. In packaging, polyolefin resins have poor oxygen barrier properties. Low dimensional and thermal stability limits the scope of polyolefin composites in automotive applications\textsuperscript{61}. One of the schemes to improve the above properties involves filling the polypropylene matrix with organically modified montmorillonite. However, the main challenge in preparing such composites is that HDPE and PP are too apolar to correctly interact with the modified layers\textsuperscript{60}. When nanocomposites are formed, they exhibit significant improvements in physical, chemical, and mechanical properties. At very low loading nanocomposites show greatly improved tensile strength, stiffness, better dimensional stability, decreased thermal expansion
coefficient, and reduced gas permeation properties in comparison with neat or unfilled polymer resin. In both academic and industrial enterprises, the study of polyolefin nanocomposites is an intense area of current interest. The driving force for such efforts is attributed to huge commercial opportunities in both automotive and packaging applications. Material design at relatively low clay loading addresses the inherent shortcomings of polypropylene resin by itself and does so with favorable cost, processing, and reduced molded-part weight profiles\textsuperscript{61}.

In spite of the large number of researchers working on preparation of polypropylene-clay nanocomposites no direct intercalation of polymer in simple organically modified layered silicates has been observed due to polymeric matrix apolarity. Two different techniques are used to overcome this problem. The first one is functionalization of the polyolefinic chain by either maleic anhydride or hydroxyl groups\textsuperscript{67}. In the second technique a commercially available organoammonium-exchanged montmorillonite is modified using an organic swelling agent (whose boiling point is situated between 100 and 200°C, such as ethylene glycol, naphtha or heptane) in order to increase the interlayer spacing. The swollen organoclay is then compounded with polypropylene in a twin-screw extruder at 250°C. The swelling agent is volatized during the extrusion process, leading to the formation of a nanocomposite\textsuperscript{68}. As one can see, both methods utilize chemicals, however, the second way is not environmentally friendly.

The most recent attempts to develop polymer/clay nanocomposites via melt intercalation in an intensive batch mixer\textsuperscript{75, 162, 163, 181} and a stationary cup\textsuperscript{164} equipped with power ultrasound were reported. However, a prolonged ultrasonic treatment (10-20

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mins) was used in these studies, apparently leading to a substantial degradation of polymer matrix. A continuous method to achieve rapid intercalation (7-21 seconds) and partial exfoliation of PP/clay nanocomposite without chemical modification of the matrix was developed\textsuperscript{167}.

In this chapter, the effect of residence time of the polymer in the ultrasonic treatment zone on controlling the structure and properties of polyolefin/clay nanocomposites is described. High density polyethylene (HDPE) and isotactic polypropylene (PP) are compared. Rheological properties, morphology and mechanical properties of the untreated and ultrasonically treated nanocomposites were studied. Similarities and differences of obtained nanocomposites are discussed based on their properties and structural characteristics.

8.2 Experimental

8.2.1 Preparation of hybrids

Cloisite® 20A natural montmorillonite modified with a quaternary ammonium salt with a cation exchange capacity of 95 meq/100g, was supplied by Southern Clay Products, Inc.

Polyolefin/clay nanocomposites with clay content of 2.5wt % were prepared by a single screw extruder with Maddock and Melt Star mixing elements and ultrasonic die attachment. The screw speed was set at 100 rpm and temperatures were 180 °C, 190 °C, 200 °C and 200 °C from the feeding section to the die zones, respectively. Two horns

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with a 4 mm gap size and 10 μm ultrasound amplitude were used. The material was ultrasonically treated in the molten state at three different flow rates of 0.25 g/s, 0.50 g/s and 0.75 g/s, corresponding to the residence time in the treatment zone of 21 s, 10 s and 7 s, accordingly.

8.2.2 Molding

Tensile bars were obtained on a Van Dorn 55 HPS 2.8F injection molding machine under the following processing conditions: a melt temperature of 190°C, a mold temperature of 25°C, an injection speed of 40 mm/s, an injection pressure of 10MPa, a holding time of 45 s, with a total cycle time of 70 s.

8.2.3 Characterization

Using a Rigaku X-ray machine operated at 40 kV and 150 mA, X-ray diffraction (XRD) patterns were obtained to determine the mean interlayer spacing of the (001) plane ($d_{001}$) for the organoclays and its nanocomposites with polymers.

Tensile measurements on injection molded samples of nanocomposites were performed according to ASTM D-638-00 using an Instron test machine Model 5567. Tests were carried out at a crosshead speed of 50 mm/min and a 30 kN load cell without the use of an extensometer. All tests were performed at room temperature and the results were the average of five measurements. The highest value of standard deviation was 11%. The rheological properties of nanocomposites were measured at 200 °C on a ARES
(Advanced Rheolmetric Expansion System). The geometry used was a parallel plate with a 25 mm diameter and a 1.9 mm gap size.

8.3 Results and Discussion

8.3.1 Comparison of process characteristics

The recorded power consumption is the total power consumption, a part of which is dissipated as heat while the rest is utilized to disperse clay filler and promote polymer intercalation into clay inter gallery spacing. However, it is not possible to determine the exact portion of power in these two cases. The only thing that can be recorded is the initial power consumption of the system when the horn is running without loading and this loss was then subtracted from the recorded values of power consumption to give the values used in Figure 8.1. An increase of flow rate leads to an increase in power consumption which is an indication that more energy is being transmitted into the system at higher flow rates. Clearly, the treatment of pure polymer requires higher energy than that of nanocomposites. Among two matrices, the HDPE shows higher power consumption, which is in a good agreement with the higher die pressure required to sustain flow, as described below.

Figure 8.2 shows the die entrance pressure as a function of flow rate. It can be seen that the pressure increases with flow rate. This is because the die pressure characterizing the resistance to flow is a function of the average residence time of the polymer in the treatment zone and the residence time is inversely proportional to the melt flow rate\textsuperscript{165}. 

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Figure 8.1 Power consumption as a function of flow rate for neat PP and PP/Cloisite 20A nanocomposites (solid symbols) and neat HDPE and HDPE/Cloisite 20A nanocomposites (open symbols).
Figure 8.2 Die pressure as a function of flow rate for neat PP and PP/Cloisite 20A nanocomposites (solid symbols) and neat HDPE and HDPE/Cloisite 20A nanocomposites (open symbols).
It is seen that HDPE shows much higher die pressure than that of PP. Unexpectedly, this is not in accord with the viscosity of systems as reported below. There are two possible reasons for such a behavior, namely, a permanent change of viscosity of melt caused by a degradation of polymer chains and a temporary change of viscosity caused by a thixotropic effect. Both these effects are evidently enhanced by the presence of clay causing enhanced cavitation. The thixotropic changes of viscosity occurring during ultrasonic treatment will recover after ultrasonic waves are ceased. This is the reason why the die pressure is higher for the neat polymer than for nanocomposites.

8.3.2 Rheology

The complex viscosity behavior of HDPE containing 2.5 wt% Cloisite 20A untreated and treated by ultrasound at different flow rates is shown in Figure 8.3. All the samples exhibit shear thinning at the frequency range accessed in these measurements. Furthermore, for the both polymeric matrices the viscosity decreases with decreasing flow rate, which can be attributed to increasing polymer degradation at longer residence times in the treatment zone. PP based nanocomposites show higher viscosity than that of HDPE based nanocomposites. It can be explained by the fact that PP matrix has lower initial value of MFI (4.0 dg/min) as compared to that of HDPE (5.0 dg/min). It may seem to be in a controversy with the die pressure data depicted in Figure 8.2 indicating that the die pressure of HDPE/clay hybrids is more than that of the PP/clay hybrids.
Figure 8.3 Complex viscosity as a function of frequency for HDPE containing 2.5 wt% Cloisite 20A untreated and treated by ultrasound at different flow rates.
Also it is seen from Figures 5.3 (b) and 8.3 that viscosity of treated samples is lower than that of untreated ones. This behavior may be due to permanent decrease of viscosity caused by polymeric matrix degradation.

8.3.3 Morphology

The XRD patterns in Figures 5.4 (a) for PP and 7.7 for HDPE illustrate the effect of ultrasound on morphology of 2.5 wt% clay/polyolefin nanocomposites prepared at various flow rates. Based on this data the inter gallery distance of clays and nanocomposites was calculated using Bragg’s Law\textsuperscript{166}. Less change in the clay’s basal spacing of PP based composites has been observed.

In particular, the basal spacing increased from 2.4 nm for pristine clay to 3.1 nm for intercalated clay in the PP/clay nanocomposite obtained at 0.25g/s flow rate. At the same time, the most significant increase in the inter-gallery distance was observed in HDPE based nanocomposites. In particular, the basal spacing increased from 2.4 nm for pristine clay to 3.8 nm for intercalated clay in the HDPE/clay nanocomposite obtained at 0.25g/s flow rate.

A significant decrease in intensity of $d_{001}$ peak suggests the presence of two distinct processes, namely, intercalation and partial exfoliation of the clay in the system. The decrease in intensity of $d_{001}$ peak is more pronounced for HDPE based nanocomposites.

These data were supported further by TEM analysis, results of which are demonstrated in Figures 4.9 for PP and 7.8 for HDPE. Unintercalated composites exhibit
the structure depicted in Figure 4.9 (a). Individual tactoids of the layered clays are visible as regions of alternating narrow dark and light bands within the nanocomposite. This regular structure was disrupted by power ultrasound, and the polymer has entered into the inter gallery spacing wherein individual clay layers are dispersed in the polymer matrix, as can be seen in Figure 4.9(b). It suggests that a partial exfoliation occurs under treatment by ultrasound. It is seen that better dispersion is achieved in HDPE matrix.

It should be noted that the length of ultrasound treatment in this particular case was 21 seconds. This treatment time for successful intercalation and partial exfoliation is substantially lower (by about two orders of magnitude) than that so far achieved in intercalation of polymer/clay nanocomposites reported earlier for a prolonged ultrasonic treatment $^{75, 162, 163, 181}$.

8.3.4 Mechanical properties

One would expect substantial improvement in the mechanical properties of intercalated/exfoliated nanocomposites when a high aspect ratio is realized. In fact, the elongation at break and toughness (the area under the stress-strain curve) are significantly increased in ultrasonically treated nanocomposites containing 2.5 wt% of clay, as evident from Figure 8.4 indicating the elongation at break as a function of flow rate. Clearly, this increase is achieved at residence times when intercalation and partial exfoliation were observed by XRD. Other mechanical properties are not substantially affected by ultrasonic treatment. This is because two competing processes simultaneously take place:
Figure 8.4 Elongation at break as a function of flow rate for neat PP and PP/Cloisite 20A nanocomposites (solid symbols) and neat HDPE and HDPE/Cloisite 20A nanocomposites (open symbols).
intercalation/ exfoliation of clay and polymer matrix degradation under the influence of ultrasound.

8.4 Conclusions

Two polymeric matrices, namely PP and HDPE, for the fabrication of clay based nanocomposites using a continuous ultrasound assisted process were compared. HDPE happened to form well intercalated and partially exfoliated nanocomposites. Two competing processes, namely, intercalation/ exfoliation of clay and polymer matrix degradation under the influence of ultrasound have been encountered.

Variations of feed rate that controls the residence time of the polymer in the ultrasonic treatment zone were studied. Results indicate that intercalation under ultrasound was higher for low feed rate. Polymer matrix degradation was substantial at the same conditions.

The elongation at break and toughness were substantially improved for both nanocomposites. To obtain enhancement in other mechanical properties further investigation of the processing conditions is needed, such as increasing processing temperature and increasing die pressure to aid the filler dispersion.
CHAPTER IX

MODELING OF THE EFFECT OF INCOMPLETE EXFOLIATION ON YOUNG'S MODULUS OF PP-CLAY NANOCOMPOSITES

9.1 Introduction

Over several decades theoretical frameworks have been developed for predicting properties of composite materials based on the properties of the pure components and the morphology of the composite. An assumption inherent in all of these theories is that each component of the composite acts independently of the other. While the general objective of such theories is to predict performance of the composite for given set of components, these theories enable a simple route for evaluation of the individual contribution of component properties such as matrix and filler modulus, volume fraction, filler aspect ratio, filler orientation, etc. Aspect ratio is an important factor in polymer nanocomposites and drives an interest in achieving a high level of platelet exfoliation.

Nanocomposite mechanics is not yet well-understood. Micromechanical methods use simplified geometries, thus neglecting complex geometrical features which could potentially be taken into account in numerical solutions of the elasticity equations by finite element simulations. They assume perfect adhesion (perfect load transfer)
between the components in a composite, thus also neglecting interfacial phenomena, which could potentially be taken into account by mesoscale simulations. Nonetheless, they are extremely useful. Since the calculations are instantaneous, they provide the ability to assess rapidly the key factors controlling the elastic behavior and to explore very large design spaces\textsuperscript{129}.

9.2 Model description

In a completely exfoliated system, the “continuum” Halpin-Tsai equations can be applied to predict the modulus of the composite material. It is often the case that one has incompletely exfoliated stacks of platelets, containing some organocation and/or matrix polymer between the platelets in each stack as evident from electron micrographs. Such stacks can contain several platelets, and the platelets within a stack can be at various distances from each other. An important issue, which may have drastic effects on the reinforcement efficiency, is the point in the interlayer expansion of a stack with a given number of layers at which a stack becomes a collection of separate exfoliated platelets of high aspect ratio of $A_f$ and Young's modulus of $E$ at a volume fraction of $\phi$, rather than behaving like a single 'pseudoparticle'. A pseudoparticle would have a lower 'effective' aspect ratio $A_f'$ (because of stacking), and a lower Young's modulus $E'$ as well as a higher volume fraction $\phi'$ (because of trapped organic fraction attached to the surface of platelet). A standard technique of composite theory that is used routinely to estimate reinforcement effects, the Halpin-Tsai equations\textsuperscript{110}, was modified by Brune and Bicerano\textsuperscript{129} to account for these effects. The resulting equations (2.8-2.12) were used in modeling.
This model accounts for the reduction of the reinforcement efficiency of clay platelets of high aspect ratio in a polymer matrix as a result of the incomplete exfoliation of platelets into 'pseudoparticle' stacks containing polymer layers sandwiched between successive clay platelet layers rather than into individual perfectly exfoliated and well-dispersed platelets. It is expected that incomplete exfoliation has a very significant detrimental effect on the reinforcement efficiency\textsuperscript{129}.

9.3 Results and discussions

To use the model described above several adjustments are needed such as conversion of weight fractions ($\phi_w$) to volume fractions ($\phi$). It is done using the following set of equations:

$$\phi_w = \frac{M_f}{M_f + M_m} \quad (9.1)$$

$$\phi = \frac{\phi_w}{\phi_w + (1 - \phi_w) \frac{\rho_f}{\rho_m}} \quad (9.2)$$

where $M_f, \rho_f$ and $M_m, \rho_m$ are weights and densities of filler and matrix, respectively.

TEM images and XRD data have been analyzed to extract the number of platelets per stack ($N=80$) and the platelet spacing ($s$). The platelet thickness ($t$) may be calculated by adding the center-to-center distance between the outer oxygen atoms in the outer tetrahedral layers of sodium MMT to twice the sum of the atomic radius oxygen. The resulting value is 0.94 nm\textsuperscript{128}. Young’s modulus of montmorillonite clay ($E_r$) has been set
to be equal to 178 GPa \(^{186, 187}\). Its aspect ratio \((A_i)\) was varied from 5 to 100 since available composite theories do not give any guidance of which aspect ratio to use when there is a distribution of lengths and thicknesses. Young’s modulus of matrix \((E_{\text{matrix}})\) was taken from Table 4.1 as for neat PP treated by ultrasound at corresponding feed rate. The input data were plug into the equations 2.8-2.12. Mathematica® 4.0 software package was used to calculate the model predictions.

Properties of materials used in calculations are summarized in Table 9.1

It is worth pointing out that because of the numerous simplifying assumptions used in the model, the comparison between simulation and experimental results should be treated only as qualitative. What is more important is the trend of simulation results when compared with experimental data.

Figures 9.1-9.3 show experimental results and theoretical predictions for Young’s modulus of 2.5, 5, 10 wt% Cloisite 20A / PP nanocomposites treated by ultrasound at different feed rates accordingly. It is seen that the experimental data are very close to the numerical simulation results in the case of aspect ratio of 5, but are much lower than the simulation data in the case of higher aspect ratio. This trend is valid for all three concentrations of clay in polypropylene matrix. Therefore, it is fair to assume that we have the case of the reduction of the reinforcement efficiency of clay platelets of high aspect ratio in polymer matrix as a result of the incomplete exfoliation of platelets into “pseudoparticle” stacks containing polymer layers sandwiched between successive clay platelets rather than into individual perfectly exfoliated and well dispersed platelets.
Table 9.1 Properties of materials used in calculations

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<thead>
<tr>
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<th>Polymer Matrix</th>
<th>Clay</th>
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<tr>
<td>Density, g/cm³</td>
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<tr>
<td>Volume fraction</td>
<td>--</td>
<td>0.0129, 0.0261, 0.0535</td>
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<tr>
<td>Young’s Modulus, GPa</td>
<td>See *</td>
<td>178</td>
</tr>
<tr>
<td>$N$</td>
<td>--</td>
<td>80</td>
</tr>
<tr>
<td>$s/t$</td>
<td>--</td>
<td>See **</td>
</tr>
<tr>
<td>$A_f$</td>
<td>--</td>
<td>5, 10, 100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flow Rate, g/s</th>
<th>Modulus at 5% strain, MPa</th>
<th>$s/t$ **</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PP *</td>
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</tr>
<tr>
<td>untreated</td>
<td>550</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>534</td>
<td>-</td>
<td></td>
</tr>
<tr>
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<td>545</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>542</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2.5/Cloisite 20A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>untreated</td>
<td>569</td>
<td>3.192</td>
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<tr>
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<td>5.0/Cloisite 20A</td>
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<td></td>
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<tr>
<td>0.75</td>
<td>569</td>
<td>2.234</td>
<td></td>
</tr>
<tr>
<td>10/Cloisite 20A</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>untreated</td>
<td>641</td>
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<td>2.234</td>
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<tr>
<td>0.75</td>
<td>618</td>
<td>2.234</td>
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</table>

156
Such stacks have a lower effective aspect ratio and a lower effective Young’s modulus than the completely exfoliated particles. It is shown that the incomplete exfoliation has a very significant effect on the reinforcement efficiency.

9.4 Conclusions

The modified Halpin-Tsai theory of composite materials has been employed in order to predict the effect of incomplete exfoliation of clay platelets on the Young’s modulus of the nanocomposites. It has been demonstrated that the assumption on reduction of the reinforcement efficiency of clay allows one to achieve a fairly good agreement between experimental and theoretical data. This simple approach involves only one adjustable parameter describing the clay’s aspect ratio. To reach the best proximity of theoretical data and experimental results one needs to modify the theory further to account for imperfect adhesion between filler and polymer and random orientation of clay platelets in matrix.
Figure 9.1 Experimental results and theoretical predictions for Young’s modulus of 2.5 wt% Cloisite 20A / PP nanocomposites treated by ultrasound at different feed rates.
Figure 9.2 Experimental results and theoretical predictions for Young’s modulus of 5 wt% Cloisite 20A / PP nanocomposites treated by ultrasound at different feed rates.
Figure 9.3 Experimental results and theoretical predictions for Young’s modulus of 10 wt% Cloisite 20A / PP nanocomposites treated by ultrasound at different feed rates.
CHAPTER X

SUMMARY

A continuous method to achieve rapid intercalation and partial exfoliation of PP/clay nanocomposite without chemical modification of the matrix was developed. Two competing processes, namely, intercalation/exfoliation of clay and polymer matrix degradation under the influence of ultrasound have been encountered.

Two clays with different levels of modification were studied. The results indicate that the intercalation under ultrasound treatment is higher for nanocomposites containing clay with lower cation exchange capacity.

Under conditions of melt intercalation the elongation at break and toughness were substantially improved. To obtain enhancement in other mechanical properties further modifications of the technique is needed, such as eliminating the compounding stage with a twin screw extruder and shifting toward a one stage process to minimize polymer matrix degradation.

Single stage process led to less polymer degradation at the fixed gap size. Variations of starved/flood feeding regimes and gap size during single stage process were studied. Results indicate that intercalation under ultrasound was higher for flood feeding and for smaller gap. Polymer matrix degradation was substantial at the same conditions.
The elongation at break and toughness were substantially improved for nanocomposites produced by the single stage process. This improvement did not exceed that of the materials derived by the two stage process. To obtain enhancement in other mechanical properties further investigation of the processing conditions is needed, such as increasing processing temperature and increasing die pressure to aid the filler dispersion.

Ultrasonic treatment improved the processing behavior of PP/PPMA based nanocomposites by reducing the die pressure. Ultrasound power consumption increased with MA modification of PP and introduction of filler.

PP/PPMA/clay hybrids underwent degradation during ultrasonic treatment. The degradation of polymeric matrix was accelerated by the presence of maleic anhydride.

The opposite effect to expected dispersion with aid of ultrasound has been encountered. Namely, collapse of intercalated structures under ultrasonic treatment was observed.

Mechanical properties of PP modified by MA and its 5 wt% clay nanocomposite untreated and treated by ultrasound were not improved. Therefore, no synergetic effect between polypropylene modification with maleic anhydride and treatment by high power ultrasound in preparation of polymer based nanocomposites has been detected.

A continuous method to achieve rapid intercalation and partial exfoliation of HDPE/clay nanocomposite without chemical modification of the matrix was developed. The effect of ultrasound amplitude on properties of obtained nanocomposites has been investigated.
Two competing processes, namely, intercalation/ exfoliation of clay and polymer matrix degradation under the influence of ultrasound have been encountered as evident from rheological data indicating highest viscosity data at 5 μm ultrasound amplitude.

Intercalation and exfoliation of clay into polyethylene have been observed by TEM and supported by XRD measurements.

It was identified that the degree of crystallinity of nanocomposites tends to decrease slightly with increase of clay contents. At the same time crystallinity decreased considerably at the ultrasound amplitude of 5 μm and increased at higher amplitudes.

Under conditions of melt intercalation the elongation at break and toughness were substantially improved. The Young’s modulus of nanocomposites increased significantly with the increase of clay loading and decreased slightly with increasing ultrasound amplitude. The yield stress of ultrasonically treated nanocomposites was more than that of the untreated samples. The yield strain of untreated nanocomposites decreased monotonically with increase of clay concentration and also with ultrasonic amplitude.

Oxygen transmission rate remains unchanged with introduction of low clay content while ultrasound treatment improved barrier properties by 20 %.

Two polymeric matrices, namely PP and HDPE, for the fabrication of clay based nanocomposites using a continuous ultrasound assisted process were compared. HDPE happened to form well intercalated and partially exfoliated nanocomposites. Two competing processes, namely, intercalation/ exfoliation of clay and polymer matrix degradation under the influence of ultrasound have been encountered.
Variations of feed rate that controls the residence time of the polymer in the ultrasonic treatment zone were studied. Results indicate that intercalation under ultrasound was higher for low feed rate. Polymer matrix degradation was substantial at the same conditions.

The modified Halpin-Tsai theory of composite materials has been employed in order to predict the effect of incomplete exfoliation of clay platelets on the Young’s modulus of the nanocomposites. It has been demonstrated that the assumption on reduction of the reinforcement efficiency of clay allows one to achieve a fairly good agreement between experimental and theoretical data. This simple approach involves only one adjustable parameter describing the clay’s aspect ratio. To reach the best proximity of theoretical data and experimental results one needs to modify the theory further to account for imperfect adhesion between filler and polymer and random orientation of clay platelets in matrix.
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