PROCESSING AND PROPERTIES OF THERMOPLASTIC NANOCOMPOSITE FOAMS AND POROUS POLYMER COMPOSITE SHEETS

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ABSTRACT

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The research work is divided into two parts. The first part is motivated by the need to produce recyclable lighter and thinner injection molded thermoplastic polyolefin (TPO) foam parts for automotive interiors by chemical foaming agent. This would require modifying the talc filled TPO compound with organoclay additive that can not only control the cell size to be smaller and more uniform, but also attain a smooth surface of the foamed parts. The objectives of this research were (1) to investigate the effect of different level of vapor phase silane coupling agent treatment on increasing the *d*-spacing of organoclay and the extent of dispersion in polypropylene; (2) to understand the relationship between melt rheology, surface appearance, foam morphology and mechanical properties of foam injection molded talc filled TPO and organoclay additive with optimized level of vapor phase silane pretreatment.

TPO nanocomposites were prepared with organically modified montmorillonite, a silane coupling agent, maleic anhydride grafted polypropylene as compatibilizer and a commercial grade TPO with 23 wt% talc loading. The organoclay was treated with 0.8 wt% of the silane coupling agent under vapor phase process to improve the interaction between the clay and the TPO to reduce the usage of low viscosity compatibilizer. The rheology of the TPO and TPO nanocomposites was examined in shear and extensional flows and this was used to select the molding temperature profile. The effects of different molding parameters- extrusion back pressure and pack pressure on the uniformity of thickness, and cell structure were examined. Stronger shear thinning behavior was conducive to a smooth surface of molded parts, allowing an operating temperature profile

close to that used for the base TPO and was crucial for both smooth surface and smaller cell size. The tensile strength, tensile modulus and flexural modulus were tested to be greater for the foam injection molded TPO nanocomposites.

The second part of the research was motivated by the need to produce a thinner battery separator for nickel-metal hydride batteries (NiMH) that had higher tensile strength and puncture strength. This was achieved by solid phase die-drawing of talc-filled polypropylene to produce stronger and porous sheet with up to 40% void fraction. The objective of this research was to explore process limits and products obtained from two different composites with different talc particle size distributions. The limiting maximum linear draw ratio without breaking was higher for the composite with the smaller mean particle size; this may be attributed to the smaller transverse dimension of stacked voids obtained with this material. At the respective limiting linear draw ratios, the porosity level is the same for both composites but the composite with the smaller talc particle sizes and higher draw ratios led to drawn sheets with greater tensile strength; this may be attributed to greater crystalline rearrangement to fibrils in this composite at higher linear draw ratio.

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Chapter 1. Introduction

Over the past decade, plastic materials have played an important role in our daily life in various applications due to the great functionality, low cost, lightweight, and easiness of processing. Porous or cellular plastic materials can reduce cost, material and energy consumption with lighter properties. The mechanical properties of porous materials are lowered by the voids generated, thus maintaining high mechanical properties for porous materials is the focus in the current research. The current research on porous materials is divided into two parts based on the different processing techniques leading to different applications. The first part of the dissertation (Chapter 3 and 4) is on foam injection molding of thermoplastic polypropylene nanocomposites; the second part of the thesis (Chapter 5) is about solid-state die-drawing porous sheets from highly filled polypropylene composites. An overview for each part will be discussed in the following sections.

1.1 Improvement in properties of thermoplastic polyolefin foams

1.1.1 Research background and motivation

Polymer foams, composed of gaseous voids surrounded by a denser continuous phase, have been widely used in our daily life. Depending on the physical property of the continuous phase, they can be classified as liquid foams and solid foams. The current research is only focused on solid foams, which have been applied to construction, packaging, automobile, furniture and refrigeration industries due to lightweight property, insulation and absorption abilities. The global market size for polymer foams was 113.85 billion USD in 2015^[1] and was predicted to reach 207.9 billion USD in 2024^[2]. The increased demand mainly comes from lightweight construction of interior and exterior materials in automobile industry and materials for insulation, floors, and pipelines in construction industry. The era of cellular polymers began from 1930s, when the first synthesized polystyrene (PS) foam was produced^[3]. Since then, polymer foams have evolved into a highly developing field. For the polymer matrix phase, both thermoplastic and thermoset materials have been widely used to produce foams: thermoplastic materials include polypropylene (PP), polyethylene (PE), poly (methyl methacrylate) (PMMA), PS, polycarbonate (PC), poly (vinyl chloride) (PVC) and polylactic acid (PLA) and thermoset materials are typically polyurethane (PU). Among all the polymer foams, PU foams have the largest portion of the foam market due to a various range of density and hardness, forming both flexible and rigid foams depending on the application. However, the cross-linked PU after reaction is not able to be recycled and results in massive hazard waste in the environment.

Thermoplastic polyolefins (TPO) meet all the requirements to replace PU foams for automotive industry. Polyolefin refers to PP and PE materials and TPO refers to blend of semicrystalline PP continuous phase dispersed with elastomeric particles, such as ethylene-copropylene (EPR) and ethylene-co-octene (EO) and have been widely used as automobile interior such as dashboard, door panels, and exterior materials such as bumper fascia, claddings^[4]; this is due to the lightweight, low cost, abrasion resistance, and enhanced impact properties compared to rigid PP materials^[5]. In order to produce lighter and thinner TPO products, one approach is to improve the mechanical property of the struts of the cell and the other is to increase the cell density, decrease the cell size and improve uniformity. The heterogeneity in cell size is greatly due to bubble coalescence with poor melt strength in the large proportion of linear PP. Extensive studies have been reported on improving the rheological behavior or melt strength of PP, including branched PP, blends of branched PP with linear PP, or PP/nanoclay nanocomposites^[6, 7]. Compared to branched PP, the addition of nanoclay can also create more nucleation sites leading to greater cell number density. Previous studies have reported that the addition of nano-scale organoclay could highly improve the polymer nanocomposites melt strength and cell density^[6-8]. The pretreatment of organoclay by vapor phase silane treatment enlarges interlayer spacing of the clay^[9, 10], and improves the dispersion of the clay in PP nanocomposites^[11]. This research primarily focuses on improving the properties of core-back foam injection molded industrial grade TPO using chemical foaming agent by modifying the rheological properties of TPO using vapor phase silane treated organoclay.

1.1.2 Polymer foams: a general introduction

Thermoplastic foams are cellular structure and the mechanical, thermal properties are mainly determined by both the matrix and the structure of cells, such as cell shape, cell density, cell size and expansion ratio (defined as the density ratio of the specimen before and after foaming). According to the dimension of the bubbles in the foams, polymer foams can be categorized as macro cellular foams with bubble diameter larger than 100 μ m, microcellular foams 1-100 μ m, ultracellular foams 0.1-1 μ m and nanocellular foams 0.1-100 nm^[12].

Based on the stiffness, foams can be classified as flexible foams or rigid foams. The flexible foams are open cell foams with cells interconnected to each other from the broken cell walls. The flexible foams have high compressibility and superb absorption characteristics, and have been widely applied to furniture, sports applications, footwears, etc. In rigid cell foams, bubbles are isolated from each other surrounded by the cell walls. The closed cell foams provide higher mechanical properties, and typical rigid foams include food and drink containers, packaging, transportation insulation materials.

A typical approach to introduce voids in thermoplastic foams is by foaming agents. Foaming agents can be either physical foaming agents or chemical foaming agents. Chemical foaming agents (CFA) are thermally unstable reactants and gas will be released when temperature reaches a critical decomposition temperature. The released gas from chemical foaming agents dissolves in the heated polymer melt under high pressure, forms nuclei and then grows into bubbles when the pressure is released. These reactions can be exothermic, or endothermic or a combination of both. The typical chemical foaming agents include azodicarbonamide^[6], benzene sulfonyl hydrazide, sodium bicarbonate and their blend with citric acid^[13]. Proper selection of CFAs based on decomposition temperature range and reaction types is crucial for a good control of the melt temperature. Physical foaming agents (PFA) are gas products at high temperature and reduced pressure under foaming conditions. The typical PFAs include gas such as N2 or CO2 or hydrocarbons such as pentane. Volatile liquid, such as Chlorofluorocarbon-type foaming agents were applied in the 90s but caused ozone depletion and thus were banned by Montreal protocol in 1987^[14]. CO₂ is the most widely used PFA because it is low cost, nontoxic, and environmentally. In 1980s, Suh et al. first innovated Mucell ® technology and applied supercritical CO₂ to create microcellular foams with cell size around 10 micron^[15].

Foaming process involves three stages: i) cell nucleation; ii) cell growth; iii) cell stabilization. Nucleation phenomenon exist in many processes, like condensation and crystallization. The nucleation occurs when the polymer melts are saturated with the blowing agents and phase separation was induced by the pressure drop. Both heterogeneous nucleation and homogeneous nucleation take place. The homogeneous nucleation is dominant for pure polymer and gas mixture with no additional filler. But heterogeneous nucleation happens at the liquid/solid

interphase with filler additives. Thus the particles with larger surface areas provide with more heterogeneous nucleation sites, and a significantly higher cell density.

In cell growth process, driven by the pressure difference between inner and outer side of the bubbles, the cell wall thickness reduces rapidly under extension; thus a strong melt strength of the material is crucial to prevent cell rupture during the cell expansion. The melt strength can be quantified by strain hardening behavior by measuring the viscosity in extensional melt flow, or extensional viscosity at different strain rates. The polymer melt with strain hardening behavior can increase the cell wall stability, prevent cell coalescence and rupture and result in an increased cell density, more uniform cell distribution and smaller cell size. For cell stabilization process, the cell size depends on the rate of solidification or crystallization of the polymer for semicrystalline material like PP compared to the rate of bubble growth. If the rate of cells growth is much higher compared to the rate of crystallization, the cells will coalesce before polymer solidifies leading to large cells. However, if the rate of the cell growth rate is much less compared to the rate of crystallization, the solidification happens before fully expansion of cells leading to small cell size.

Foams can be produced by either non-continuous methods, such as batch foaming, foam injection molding (FIM), compression molding foaming or continuous approaches such as foam extrusion. Batch foaming process is in a heated autoclave with pressurized CO_2 or N_2 . After saturation at the desired pressure and temperature, the pressure is released at a set releasing rate and the cells grow rapidly during this process. Extrusion foaming is driven by the released pressure drop at extruder die exit leading to bubble expansion. Compared to batch foaming and extrusion foaming, foam injection molding (FIM) has attracted much attention to researchers because its ability to produce parts in varied shapes in short production cycles^[16]. Extruded polymer melt with dissolved gas is injected into a heated mold, following by filling, packing and the ejection stage.

Conventional injection molding foaming can be categorized into low pressure FIM^[17] and high pressure FIM based on the pressure inside the mold^[18, 19]. In low pressure FIM, the shot size is less than the cavity (short shot) and the bubble nucleation and growth happen once entering the mold due to the lower pressure compared to the pressure inside the bubbles in the mold. As the filling goes on, the bubble size is greater near the end of the fill position compared to the position near the gate due to the reduced pressure drop rate as mold cavity is filled. Even though the bubbles are not uniform, up to 40% void fraction of the foam parts can be attained^[18, 19]. In high pressure FIM or full shot process, the bubbles start nucleation when the polymer melt enters the mold but the high pressure in the cavity or pack pressure in packing stage can redissolve "gate-nucleated bubbles". The driving force of bubble expansion is driven by the shrinkage of the polymer melt during solidification process. Thus the cell size is more uniform in high FIM, but the density reduction is restricted to 5-10%, and the pressure drop is low, especially in amorphous polymers^[19].

One side of the mold opening, or core-back stage, after the packing stage is applied to produce polymer foam with more uniform structure and greater density reduction at a set speed and distance^[16]. The core-back foaming process is illustrated in Figure 1.1.



Figure 1.1 Schematic of core-back injection molding foaming

The abruptly reduced pressure during the cavity expansion allows rapid growth of bubbles and the density of the foam could be controlled by the distance of the opening^[16]. The disadvantage of the core-back FIM is that the bubble expansion is only along the mold opening direction. If the geometry is complicated and the areas parallel to the mold opening direction will not be foamed properly. Studies have been reported on core-back FIM of TPO ^[20, 21], PP ^[22, 23] and talc and fiber filled PP^[16, 24], PP/PTFE nanocomposites^[25], talc and clay filled^[26-28] and polystyrene^[19]. The TD-ND cross section of the molded part has a sandwich structure with skins on the top and bottom surface and foam structure in the center. This is due to that the mold temperature is typically much lower than the melt temperature, and the bubbles were not able to expand before the polymer solidifies near the mold wall. And the cell size is usually smaller near the skins compared to the center location of the foam sandwich.

1.1.3 Polymer nanocomposites

Polymer nanocomposites are polymer matrix with dispersed particles with at least one dimension at nano-scale. Polymer nanocomposites have been widely used in automotive, packaging, construction and electronic industries, due to the improved properties like gas and liquid barrier, mechanical, thermal, electric and magnetic properties with a low filler loading. Compared to traditional composites filled with high loading of micron-sized particles, the nanocomposites do not sacrifice the density and opacity compared to the base polymer. The leading research in nanocomposites include silicate nanoclay, carbon nanotubes and fibers, graphene nanoplatelet and cellulose fibers. Among all the fillers, nanoclays are the most widely studied due to their high aspect ratio up to 100 to 200 and large surface area for polymer interaction, low cost and availability^[29]. The tensile modulus of the clay is between 178-265 GPa with the typical lateral dimension of 100-200 nm and thickness of clay platelet 1 nm and the distance of

interlayer is around 1nm^[29, 30]. Even though both tensile modulus and surface area are smaller for nanoclay compared to graphene nanoplatelet, the processing conditions are much more friendly for clay because the graphene nanoplatelet bulk density is low and requires higher shear speed^[29].

The era of polymer/clay nanocomposites started with technology invented by Toyota, using polyamide 6 and organoclay in 1980s^[31, 32]. With only 5 wt% clay loading, the tensile modulus increased by 60% and the flexural modulus increased by 126%^[31, 32]. Since then, clay has been used to produce different kinds of nanocomposites with PLA, PS and PMMA, etc. The nanoclay is composed of alternating layers of tetrahedral silica sheets SiO₂ and octahedral aluminum sheets AlO₆ in different ratios. The most common form of clay is montmorillonite, which has two layers of tetrahedral silica sheet sandwiching one layer of octahedral alumina sheet with the ratio of 2:1^[33] and belong to 2:1 phyllosilicates. Other 2:1 phyllosilicates family members include: sepiollite (nano-fibers) and halloysite (nano-tubes) together with montomorillonite (nano-plates)^[33]. These layers are weakly bounded by van der Walls forces. Charge deficit was caused by partial isomorphous substitution of Si⁴⁺ ions by trivalent metal cations and Al³⁺ ions by divalent metal cations^[10]. In order to balance the charge deficit, a great number of exchangeable ions like Ca²⁺ and Na⁺ are fixed in the interlayer space of montmorillonite by electrostatics^[10].

The properties of nanocomposites with clay are strongly dependent on the degree of dispersion of the clay in the system. Several methods have been used to detect the dispersion of the clay in the system: Transmission electron microscopy (TEM), X-ray diffraction (XRD), etc.^[34]. The degree of dispersion of the layered silicates are categorized into intercalated or exfoliated based on whether the interlayer of the silicates is separated- see Figure 1.2. In intercalated structure, polymer chains enter the interlayers of the silicates expanding the galleries but the adjacent

platelets still keep the ordered structure; for exfoliated structure, the ordered platelets structure breaks and reaches a complete mixer of polymer and clay.



Figure 1.2 Classification of layered silicates and polymer based on the degree of dispersion

Several methods can be used to produce polymer nanocomposites: solvent blending, insitu polymerization and melt blending method. Solvent blending method involves nanoparticles dispersed in a solvent with polymer matrix dissolved. The polymer chains adsorb to the surface of nanoparticles in the solvent but this method has two disadvantages: one is that the nanoparticles tend to re-agglomerate after removing the solvent and the other is the costly large amount of solvent waste generated. Melt blending method is the most efficient way of dispersing nanoparticles, and will be used in this research.

The mechanism of melt blending is "peeling" of layered silicates. The compounding of PP and nano involves two types of mixing: distributive mixing and dispersive mixing. In distributive mixing, the aggregated clay tactoids or stacks are broken into single tactoids; whereas, in dispersive mixing, the single tactoids are further broken into clay nanoplatelets^[35]. And PP chains will penetrate between the closely stacked interlayers overcoming the Van der Waals force.

Several approaches were developed to ensure good dispersion of the clay. First, the chemical incompatibility between the clay and the PP can be overcame by chemically modifying the clay: exchanging the hydrophilic ions in the interlayers by alkylammonium ions. The alkylammonium ions with greater sizes compared to the inorganic ions can expand the distance of interlayers.

Another approach to increase the polypropylene and clay interaction is to make a blend of PP matrix and a compatibilizer to increase the miscibility of nonpolar polymer matrix like PP with clay. Previous research has reported that compared to amine functionalized PP (PP-g-NH₂), maleic anhydride grafted polypropylene (PP-g-MA) attributes to a much more effective exfoliation of clay and improved tensile modulus^[36]. Several factors will affect the exfoliation of the clay in the PP matrix including the compatibilizer to clay ratio, the molar ratio of maleic anhydride group to compatibilizer chain, and the molecular weight of the PP-g-MA^[30, 37-41]. The PP-g-MA to clay ratio was reported to be at least 2:1 in order to achieve a good dispersion^[37]. The shear stress, increasing shear time, and lower the mixing temperature has been reported to improve the intercalation and exfoliation of the clay in the PP matrix^[37].

Since the viscosity of the compatibilizer is much lower than the polyolefin matrix, the amount of compatibilizer used should be as low as possible in order to maintain good mechanical properties for the products. An approach is to pre-treat the organoclay with silane coupling agents before compounding. Studies have been reported that silane coupling agents could improve the interaction of the clay and the polymer by attaching to two interface sites: either at the edges^[42-44] or the faces^[44-47] of the clay (see Figure 1.3).



Figure 1.3 The interaction of silane coupling agent with clay in comparison with clay without silane treatment.

The silane grafting reaction can happen either in a solvent base (wet process) or from the silane vapor saturation (dry process) at the boiling point of the silane coupling agents. In wet process, silane molecules could easily hydrolyze in the solvent and then condense among themselves to form various sizes before entering the interlayer of the clay, and only polymers with appropriate size can intercalate into clay galleries ^[9, 10]. Another reason is that the silane hydrolysis can happen in the interlayer of the clay and simultaneous condensation of the silane molecules and silane molecules bonding to the adjacent layers face sites can fix the gallery height of the clay^[48]. In dry process, the single silane molecules enter the gallery first, followed by hydrolyzation and condensation; thus more effective silane molecules can penetrate into the galleries even at a low level of silane coupling agents^[9].

For clay filled nanocomposites, the location of clay is crucial for the foaming process because the bubble growth process tends to occur in the phase with lower viscosity. Even though study has been reported that for batch foaming process, the bubbles could be all concentrated to the rubber phase due to a much greater solubility of the CO₂ in the rubber phase^[49]. The clay particles locations in TPO depend on the elastomer type, presence and type of compatibilizer, and preparation approach of TPO (through in-reactor polymerization or physical blending)^[5, 50, 51]. For TPO where PP is the main phase with 30% dispersed EOC rubber phase with no compatibilizer, the clay was reported to be in the rubber phase^[50]. Studies have been reported that the clay was observed in PP matrix with the addition of PP-g-MA as the compatibilizer in TPO ^[5, 50]. When the compatibilizer was maleic anhydride modified EOC (EOC-g-MA), the clay was reported to be in the addition of maleic anhydride modified EOC as the compatibilizer by Bagheri-Kazemabad *et al.* ^[50]. The clay was discovered in EOC phase with EOC-g-MA as compatibilizer even when the continuous phase is the EOC dispersed with PP phase by Austin *et al.* ^[52].

The addition of clay also modifies the morphology of the rubber phase. Studies have been reported that the addition of montomorillonite decreases the rubber particle size by preventing the retarding coalescence of the rubber particles in injection molding process.^[5, 51, 53]. As a result, the tensile strength modulus was reported to be increasing with the clay and PP-g-MA additive^[51]. This is attributed to the reinforcing effect of the clay on PP matrix in TPO. The elongation at break decreases as the PP-g-MA to clay ratio increasing due to the low viscosity of the PP-g-MA. Tiwari *et al.*^[51] reported a lower impact property was observed with the elongation at break decreasing as the PP-g-MA and clay loading increasing with a 1:1 ratio because PP-g-MA has a low viscosity. The impact property of the TPO material is enhanced due to the rubber particles. The impact strength increases and levels off as clay loading increases from 0 to around 3 wt% and increases slightly as the PP-g-MA to clay ratio increases^[51].

1.1.4 TPO and TPO nanocomposites foam

The injection molded TPO foam was reported to attain bubble size between 40 μ m-100 μ m and when using Mucell® technology^[20] and core-back FIM. For talc filled TPO, Yetkin *et al.* reported that the cell size was reduced to be 175-235 from 360-550 micron^[54] with the addition of 20 wt% talc filler to TPO by conventional FIM using chemical blowing agent. Santoni *et al.* ^[4] reported that an increased cell density with smaller cell size was achieved with the addition of 10 wt% talc and PP-g-MA. For clay filled TPO system, Hwang *et al.* ^[55] reported cell size reduction from 100-110 μ m to 70-80 μ m with the addition of nanoclay using Mucell® technology without core-back stage.

The surface appearance of the foam injection molded parts is of great importance to industrial products. Unlike the typical flow marks or "tiger stripes" caused by the rapid retraction of the elastomeric phase^[56], jetting and silver streaks were reported on the surface of the foam injection molded TPO and talc filled TPO parts^[57]. The inclusion of PP-g-MA as a compatibilizer for talc filled TPO^[4], and lower melting temperature, proper selection of endothermic CFA helps with reducing the silver streaks^[57]. The commercial TPO contains around 20 wt% talc to reduce the shrinkage and surface unevenness. This is because a greater plane area of talc has better effect on attributing to a smoother surface compared to other types of filler like organoclay or silica spheres ^[58]. The glass fiber has also been reported to be more effective to prevent shrinkage of injection molded PP compared to nanoclay ^[59].

Non-uniform and large bubble size was observed in linear polypropylene foams, leading to low tensile and flexural properties. In order to better control the uniformity and size of bubbles, a high extensional viscosity is in favor of enduring the fast bubble expansion. The foams of both PP and TPO with the addition of organoclay have shown tremendous increase in cell density and reduction in cell size in both extrusion and injection molding foaming^[7, 60]. The cell size distribution is also more uniform. The advantages of adding organoclay for foaming include: i) More nucleation sites are formed by adding nano-scale particles with large surface areas, leading to improved cell density. ii) Improvement in melt strength, preventing bubbles from coalescence, and contributing to cell density and reducing cell size^[6].

The tensile strength, tensile modulus, flexural modulus, and impact strength of the polymer foams are related to both the foam structure, including density and porosity and also the property of the cell walls. Gibson *et al.* has related the tensile modulus and tensile strength ratio of the foam and the unfoamed polymer material to the polymer fraction in the cell wall, and the density ratio [61, 62].

$$\frac{E_f}{E_p} \approx C_1 \left(\emptyset \frac{\rho_f}{\rho_p} \right)^2 + C_2 (1 - \emptyset) \left(\frac{\rho_f}{\rho_p} \right)$$
(1.1)

$$\frac{\sigma_f}{\sigma_p} \approx C_3 \left(\emptyset \frac{\rho_f}{\rho_p} \right)^{3/2} + C_4 (1 - \emptyset) \left(\frac{\rho_f}{\rho_p} \right)$$
(1.2)

Where E_f is the tensile modulus of the foams, E_p is the tensile modulus of the unfoamed polymer and ρ_f is the density of the foam, ρ_p is the density of the unfoamed polymer. Ø is the fraction of solid in cell struts, σ_f is the tensile strength of the foams, σ_p is the tensile strength of the solid part. C_1, C_2, C_3, C_4 are constants. Wong *et al.* ^[21] changed the superscript to be ½ instead of 2 for the tensile modulus equation 1.1 to relate the tensile modulus ratio of the foam and the unfoamed injection molded TPO parts. However, few studies reported the connection of the pore dimensions and the tensile properties.

1.1.5 Importance of crack length on mechanical properties

The voids in the polymer foams are defects or the weak regions during tensile tests. The failure of cellular materials is attributed to the crack propagation in transverse direction perpendicular to the drawing direction- see Figure 1.4. The TD dimension of the largest pore in the foam is the crack length, which is typically the coalesced bubbles in the center of the foamed parts. The crack will spread only if the total energy of the system is lowered nearby. From the total energy calculation considering elastic strain energy and the work of crack formation, the criterion for the crack propagation can be represented by the stress intensity factor *K* in the following inequality^[63]:

$$K = \bar{\sigma}(\pi a)^{\frac{1}{2}} \tag{1.3a}$$

$$K > K_c \tag{1.3b}$$

Where $\bar{\sigma}$ is the draw stress along the drawing direction, *a* is half of the crack length. When *K* is above a critical value K_c , the crack propagation will occur. Thus the foam part with a smaller crack length or smaller TD dimension of pore could endure a higher draw stress without crack propagation, leading to greater tensile strength and the crack may not spread if the draw stress is low.



Figure 1.4 The schematic of the crack length in transverse direction in porous sheet

1.1.6 Research objectives

This research is motivated by the demand of lighter and thinner foam injection molded in automotive interiors industry. This requires compounding TPO with organoclay additive to better control the cell structure including a greater cell density, lower and more uniform cell size and attain surface smoothness of the molded plaque parts simultaneously. A vapor phase silane coupling agent treated clay will be used to reduce the amount of low viscosity compatibilizer usage to prevent reduction in mechanical properties of the final molded parts. The objectives of this work include:

- 1) to investigate the effect of different level of vapor phase silane coupling agent treatment on increasing the *d*-spacing of organoclay and the extent of dispersion in polypropylene.
- 2) to understand the relationship between melt rheology, surface appearance, foam morphology and mechanical properties of foam injection molded talc filled TPO and organoclay additive with optimized level of vapor phase silane pretreatment.

1.2 Solid state die-drawing

1.2.1 Research background and motivation

The market of hybrid electric vehicles (HEV) or electric vehicles (EV) have been growing tremendously in the past decades and boosting the market of batteries. Two types of batteries have been used for EV cars – lithium ion batteries in Tesla, Nissan Leaf etc. and nickel metal hydride batteries in Toyota Prius, etc. The lithium ion batteries have a greater energy density, higher operation voltage compared to NiMH batteries. However, more than 10 million hybrid electric vehicles on the road are powered by nickel-metal hydride batteries (NiMH). Compared to lithium ion batteries, the NiMH batteries have a wider operation and storage temperature range, a high energy density and a long life time^[64]. The separator membrane in a battery is used to separate the

cathode and the anode, hold electrolyte in the pores and allow ion transport between the two sides of the battery. One way to increase the energy density of the NiMH batteries is to use more compact batteries like pouch cells with thinner battery separator but remain high mechanical properties.

The conventional NiMH battery separator is nonwoven fabric of polyolefin fiber that can be produced by dry casting, wet casting or melt blowing^[65]. The wet-laid process, similar to paper making process, is a typical method for making commercialized 400 μ m thick plasma treated PP/PE/PP nonwoven of polyolefin fiber. The surface of the membrane is plasma treated to be hydrophilic and compatible with the KOH electrolyte in NiMH battery. The nonwoven fabric has labyrinth or irregular pores with micron sized pores (see Figure 1.5(a)) and the tensile strength of the material is around 17 MPa. One of the approaches to produce lithium ion battery separator is via dry process-uniaxial stretching the PP or PE casted film from several hundred micron down to 20-30 micron thick membrane with sub-micron sized pores. The porous film has a porosity of around 40-55% with a tensile strength of around 100-160 MPa in MD and 13-14 MPa in TD^[66] – see Figure 1.5 (b).



Figure 1.5 The scanning electron microscopy of (a) nonwoven fabric for NiMH battery^[67] and (b) Celgard 2400 battery separator for lithium ion battery^[65].



The film stretching method is not applied to produce NiMH battery separator because the pores are only 10-50 nm diameter from film stretching and the ionic conductivity is too low for KOH electrolyte.

The phenomena of submicron pores generated by stretching of solid neat PP under melting temperature is called cavitation. These elliptical pores are from deformation of stacked crystal domains or row-nucleated lamellar structure (see Figure 1.6) for precursor PP film, followed by room temperature stretching first, and then higher temperature stretching to increase pore dimension ^[68]. As opposed to spherulitic lamellae^[69, 70], the row-nucleated or stacked lamellar structure is formed due to stress induced crystallization under high melt stretch rate to form precursor PP film^[70]. People have found that a high molecular weight of the polymer is in favor of the growth of the row-nucleated lamellar structure^[71].



Figure 1.6 The row-nucleated lamellae structure.

When the lamellae is weak or defected, plastic deformation of the crystals is dominant and when the lamellae is thick and strong, the breakage of lamellae followed by the stretching of amorphous chains in the amorphous region contribute to cavitation^[72, 73]. The cavitation process only happens when the temperature is between 25-30°C and disappears at elevated temperature like 70-100°C^[74].

Previous research has shown that the filled polypropylene could be used as the precursor film for stretching to form porous sheets. Debonding of the particles instead of cavitation will occur when the particle size is above a critical value. This is because the load on the composites cannot be transmitted from the continuous polymer phase to the dispersed filler phase and the interfacial stress increases until the particle debonds. Mizutani *et al.* have performed biaxial stretching of filled PP with CaCO₃ or SiO₂ film to produce membranes and the pores are controlled by the filler content, particle size and degree of stretching^[75]. The median pore size was around 1.4 um when the average diameter of the filler average was 3 μ m with a thickness of between 120 to 200 μ m. The permeability water vapor was slightly greater compared to Celgard 2500^[75]. Thus it has been mostly applied as the packaging material due to the good barrier properties of water vapor moisture. The stretching process was as great as 280% in MD but when the filler size increases, the limiting stretching ratio will decrease and the mechanical properties will not be

increased as much because when the larger filler will lead to greater voids, and when the elongated pore size is greater than the critical defect size, then the crack initiation and propagation will occur. Thus an approach that allows for stretching to a greater stretch ratio without breakage should be used when the desired pore dimension is around 8 microns comparable to nonwoven fabric with larger fillers.

Solid state die-drawing of neat or unfilled semicrystalline polymer at elevated temperature below melting temperature was first invented by Dow chemical in 1970s. It is well known that the die-drawn polyolefin and acetals attain a 10-20 folds increase in tensile strength and tensile modulus^[76-79]. This kind of increase in the tensile strength and modulus are related to the crystallinity increase and orientation of crystals of the polymer. Using filled polyolefin instead of unfilled semicrystalline polymer for this process can create porosity up to 40-50%^[80]. Since the size of voids generated by the debonding of particles in transverse and thickness direction are constrained by the particle size, the pore size distribution could be better controlled with the properly selected filler size. This technique has been used to replace wood for furniture and construction materials such as docking boards *etc.* with a thickness of 2 mm thick or thicker. However, no one has used this method to make thin membranes like battery separators. Thus the primarily focus of this research is to develop a battery separator to be thinner but remains high tensile strength using die-drawing technique.

1.2.2 Die-drawing process

The die-drawing process is a technique that combines the free drawing and the deformation through a converging die with a decreased area from the inlet to the outlet- see Figure 1.7. A neat or polymer composites is extruded and then fed into a heated oven at 30-40 °C below the melting

temperature, annealed for half an hour to 2 hours depending on the thickness of the material. The deformation process happens not only in the converging die but also in the free draw region.



Figure 1.7 Schematic of die-drawing process.

Depending on the thickness of the material, the billet contacts the die at different location inside the die. The cross-section area of the billet divided by the area of the converging die exit is defined as the nominal draw ratio. The degree of deformation or strain can be quantified by draw ratio, which is defined as the speed of the speed at a certain downstream location u_1 divided by the speed of the billet where the billet first contacts the die u_0 . The speed of the billet at location closest to the puller will be greatest and gradually decreasing as moving closer to the die. Draw ratio may be evaluated with the following equation based on a steady state mass balance:

$$DR = \frac{u_1}{u_0} = \frac{\rho_0 A_0}{\rho_1 A_1} \tag{1.4}$$

Where ρ_0 and ρ_1 are the density of the billet before and after drawing, and A_0 and A_1 are the cross-section area of the billet before and after drawing. Linear draw ratio is another terminology for strain following the equation:

$$LDR = \frac{L_1}{L_0} \tag{1.5}$$

where L_1 and L_0 are the distance between two marks on the surface of the billet after and before drawing. Linear draw ratio has been used for film stretching process. For thin billets, the linear draw ratio can be approximated to be the area reduction ratios in eqn. 1.3. For die-drawing process of neat polymer, people have used cross section area ratio of the undrawn and drawn billet to be the draw ratio without considering the density reduction^[77, 79, 81]. It has been known that the tensile strength and tensile modulus increases as draw ratio increases^[77, 79, 82]. For a certain draw speed of the puller, the draw ratio is increasing along the pulling direction while the maximum draw ratio or final draw ratio is reached at the position close to the puller^[79]. The maximum draw ratio reached near the puller increases with draw speed but levels off with higher draw speeds. The maximum draw ratio of neat polymer has been reported to increase with crystallinity and decreases with the molecular weight of the initial polymer^[82]. The draw stress, or force divided by the cross section area of the billet applied on the billet increases linearly with the draw speed of the puller^[83]. The billet will break if the draw stress exceeds the build-up in tensile strength of the material due to crystalline rearrangement to fibrils. The water or air cooling in free draw region is to prevent breakage of the billet, especially at the die-exit region where the stress is concentrated without enough strength build-up^[77].

1.2.3 The structure of PP composites during die drawing process

Several processes occur simultaneously during the die-drawing process. During the half an hour to two hours annealing process, the crystallinity of the polymer composites is increased. During the deformation of neat polypropylene both inside and outside the die, the crystalline region experience spherulites break up lamellae and fragments as well as disengagement of amorphous chains recrystallization to form fibrils. When particles are filled in the polymer, the density of the drawn material will be lowered due to the debonding process.

Polymer crystal structure and crystallinity

The isotactic polypropylene homopolymer could form monoclinic α -form, hexagonal β form, or orthorhombic γ -form crystals under different cooling conditions^[84]. The most stable form is α -form crystals with a monoclinic unit cell and adjusted orthogonal crystal axis a^* , b and c. The crystalline region of the extruded neat PP is dominated by the spherulites or cross-hatched structure with radial and tangential lamellae surrounded by amorphous region under low stress induced cooling process as opposed to a row-nucleated structure under high stress induced cooling for PP film stretching process. The presence of micron sized talc in PP composites enhances the crystallization start temperature and changes the morphology of the polymer with smaller spherulites as well as transcrystalline (columnar crystal) normal to the interface of the talc flakes^{[85-} ^{87]}. This is due to that the talc particles serve as nucleating agents, and high density of heterogenous nucleation occurs on the surface of the talc and restricts the lateral growth of the crystals^[88, 89]. The topology of the filler is crucial for transcrystalline formation and wood lignocellulose or glass fiber could also form transcrystalline only with certain treatment on the surface or with additives^[88, 90]. As the loading of talc increasing, it has been reported that the *b*-axes of the crystals is oriented along the normal direction or thickness direction up to 20 wt% and level off^[91-93]. Most of the transcrystalline is α -form, but β -nuclei could be generated when the cooling rate is fast during the coextrusion process, which can improve the tensile and impact properties^[94]. Annealing process for neat PP has been reported to increase crystallinity^[84, 95-97], thickening of lamellae^[84, 95, 97-100] as well as reducing the defects^[84, 95, 98]. The addition of talc filler has shown to enhance the crystallinity of the composites as the annealing time increases but the greatest transition happens in the first hour^[97, 101]. The increase in crystallinity is due to that the tie chains in amorphous region can fold and recrystallize into lamellae when annealing between the crystallization temperature

and the melting temperature, when a thermodynamic lower energy level is preferred ^[84, 95]. A higher level of crystallinity is in favor of the polymer orientation in the die-drawing process as the tensile strength and tensile modulus are enhanced for the PP after annealing^[84].

Polymer orientation and fibril formation

During the die-drawing process, the solid state polymer matrix undergoes several stages: i) elastic region ii) yielding point iii) post-yield region. The yield stress of both amorphous and semicrystalline polymer is related to temperature and the strain rate by Eyring's model^[102], as is given in equation:

$$\left(\frac{\sigma_y}{T}\right) = \left(\frac{2}{V^*}\right) \left[\left(\frac{\Delta H}{T}\right) + 2.303 R \log\left(\frac{\dot{\varepsilon_y}}{\dot{\varepsilon_0}}\right) \right]$$
(1.6)

Where σ_y is the yield stress, T is the temperature, V^* is the activation volume, ΔH is the activation enthalpy and $\dot{\varepsilon}_y$ is the strain rate at yield, and $\dot{\varepsilon}_0$ is a constant. The yield stress is greater at a greater strain rate or lower temperature. The polymer will yield at a lower macroscopic stress due to stress amplifying effect- a greater stress in the polymer near the particles ^[103].

Different mechanism dominates for polymer during solid-state drawing process depending on the drawing temperature. It has been reported that at lower drawing temperature(<60°C), the mechanism of polymer crystalline rearrangement at high strains is different than that at higher temperature^[104]. Only the intra lamellae happens and the reorientation of the broken lamellae occurs at high strain. Above 60°C, the stress induced recrystallization of amorphous chain to transform into folded-chain crystal was achieved at temperature above 60°C. It has been reported by Chen *et al.* that finer distinction between 60-120°C and 120-150°C exits: between 60-120°C, the inter lamellae slip dominates and the micro fibril forms after yield point due to decreased interfacial energy; between 120 °C and 150 °C, the stress induced entropic reduction of amorphous
phase leads to recrystallization of lamellae for the amorphous phase and the fibrillar crystal is formed as a result of the thermal effect^[105]. During die-drawing process of talc filled PP, both spherulites and transcrystals were broken up into lamellae due to shearing on intra lamellae and fragments due to shearing on inter lamellae and finally fibrils were formed. However, transcrystals breakage happens at higher strains during the drawing process^[106]. Ward *et al.* reported that above the glass transition temperature, crystalline orientation for semicrystalline polymer is a function uniquely defined by the draw ratio, regardless of the crystallinity and the lamellar structure^[107].

Debonding of particles

The density reduction involves three stages. First, the polymer debonds from the particles when the adhesion of the particle and the filler is weak. The macroscopic stress applied to the polymer matrix could not be transferred by the more rigid particles, and stress is concentrated on the tips or edges of the particles along the drawing direction. When the potential energy near the particles is greater than the work of adhesion, voids will be initiated around the tips or edges of the particles. The debonding process happens only in the elastic region before the yielding point of the polymer is reached^[108, 109]. Then the voids will be elongated as the draw ratio increases. The void dimension in TD and ND direction will be restricted by the width and thickness of the particles. The debonding region will start to enlarge until around 116° of the 2θ at each pole of the particle^[110]- see Figure 1.8.



Figure 1.8 Schematic of debonding or void initiation.

The debonding stress is predicted using the energy balance between the potential energy near the debonded particle surface and the work of adhesion between the matrix and filler phase by Vollenberg *et al.*^[110] following equation:

$$\frac{\sigma_d^2}{2E} |\Delta V_d| = W_A |\Delta S_d| \tag{1.7}$$

Where W_A is the work of adhesion between the matrix and the filler, E is the matrix modulus, ΔV_d is the debonded volume, ΔS_d is the debonded surface area.

Sudar *et al.* ^[111] reported that the part of the debonding stress comes from the residual thermal stress from the cooling of the composites during compounding and the debonding stress could be predicted in the model following equation:

$$\sigma_d = -C_1 \sigma_T + C_2 \sqrt{\frac{W_A E |\Delta S_d|}{|\Delta V_d|}}$$
(1.8)

Where σ_T is the residual thermal stress, C_1 and C_2 are constants, W_A is the work of adhesion between the matrix and the filler, E is the matrix modulus, ΔV_d is the debonded volume, ΔS_d is the debonded surface area. For spherical fillers, the ratio of ΔS_d and ΔV_d is 6/R when fully debonded and $6/R \sin\theta$ when partially debonded. The debonding stress is greater for smaller particles.

1.2.4 Importance of pore dimension on die-drawing process

Fracture during drawing can be illustrated in the eqn. 1.3. The TD dimension of pore during the drawing process has been represented Figure 1.9. The composites with larger pore in TD dimension or crack length developed will start to propagate under a lower draw stress, leading to breakage during drawing process.



Figure 1.9 The schematic of voids generated during debonding process with the crack length perpendicular to the machine direction.

1.2.5 Research objectives

The motivation of this research is to achieve thinner but stronger porous polypropylene with greater strength than currently available. Thin porous sheets are commonly used as battery separator. The stiffness and mechanical strength of the separator are tied to the thickness as well as the porosity. As the thickness is lowered, there is a greater need for greater tensile strength.

It is well known that the die-drawing process could increase the stiffness of unfilled semicrystalline material by 10 folds. The die-drawing of filled polymer leads to expanded composite materials with lower density and improved mechanical properties. During die-drawing process, the higher tensile properties were achieved with higher draw ratios at higher speeds. However, as the thickness of the billet is lowered, the material will break if the draw stress exceeds the tensile strength of the material. The tensile strength is dependent on the crystalline rearrangement and the porosity development. The mechanism of the breakage is the crack propagation along the transverse dimension. The crack propagation will occur Thus the critical crack length is much smaller during die-drawing process and is determined by the largest pore dimension in TD. Because the TD dimension of pore is restricted by the particle size, the particle size is crucial but few studies reported the pore size effect on the die-drawing process. The objective of this research is to examine the die-drawn products of talc filled PP composite sheet with two different grades of talc with different mean particle size effect on the die-drawing process.

Chapter 2. Experimental Procedures and Materials

2.1 Materials

Two different grades of isotactic polypropylene were used for die-drawing process: PP 5D37 (from Dow Chemical Co.), with a melt flow index of 2.8 g/10 min (230° C/2.16 kg) and PP 6025N (from Braskem), with a melt flow index of 2.5 g/10 min (230° C/2.16 kg). Both of the two polypropylenes have a melting temperature of 168°C. The grades of talc in the two composites were Jetfil 290 (from Imerys Marble Inc.) with a median particle size of 8.5 µm, and BT2213 (from IMI FABI) with a median particle size of 10µm.

A polypropylene served as matrix in nanocomposites was Profax 6523 from Basell, with a melt flow index of 4 g/10 min (230°C/2.16 kg). A thermoplastic polyolefin (TPO) used in nanocomposites was ADX 5349 (from Advanced Composites, Inc.).

A maleic anhydride modified polypropylene (PP-g-MA) used as the compatibilizer in nanocomposites: copolymer Exxelor 1015 (from ExxonMobil Chemical Co. Mw = 122,000, MA content = 0.42%) with a melting temperature of 145°C. The organoclay used in the nanocomposites was montmorillonite clay-- I.44P (from Nanocor, Inc.). The reactive silane coupling agent used for silylation was 2-aminoethyl-3-aminopropyl methyldimethoxysilane Dynasylan 1411 (from Evonik, Co.).



Figure 2.1 Chemical structure of 2-aminoethyl-3-aminopropyl methyldimethoxysilane.



Figure 2.2 Reaction schematic between silane treated clay and the maleic anhydride grafted polypropylene.

2.2 Die-drawing Procedure

The materials were compounded with a twin-screw extruder at 180°C and extruded to form billets with the help of Eovations, LLC, Bay City, MI. The billet thickness ranged from 4.0 to 4.6mm and the die had an exit gap of 2 mm. The width of the billets was not restricted by the mold and remained unchanged in the die at 40mm but was reduced in the free draw region outside the die to 30 mm.

The die drawing experiments were carried out at our laboratory at Michigan State University. 80 cm long sections of billet were preheated in an oven (Grieve model MT0559) and then pulled through a heated die next to the oven by a Conair belt puller. The billet exiting the die was cooled by compressed air streams in the free draw region.

2.3 Nanocomposites Preparation

The nanocomposites for the scope of this research was prepared by melt mixing technique, and Banbury batch mixing and twin- screw extrusion were both used for this study. Before mixing, the clay and PP-g-MA were dried overnight under vacuum to remove any possible moisture before using for compounding.

For lab-scale nanocomposite samples, a 75 cc Banbury batch mixer from C.W. Brabender Instruments, Inc. Banbury and a 220 cc HAAKE Polylab OS Banbury batch mixer were both used for compounding process depending on the amount of sample needed. A two-step mixing procedure was used: the "masterbatch" -- a high concentration of clay and PP-g-MA with some amount of matrix polymer was made first, then a "letdown" procedure was performed to dilute the clay amount to the desired loading. Research has shown that the two-step procedure is helpful for getting a good dispersion of the clay^[112]. The mixing process was under 180°C and 150 rpm 8 min for masterbatch (mixing the clay and PP-g-MA with 20% of the matrix material) while 10 min for letdown (Diluting the masterbatch with matrix material to the desired loading of clay). Around 50 g of material was used for masterbatch and letdown for 75 cc Banbury mixer. 200 g of material was used for letdown while 220 g of material was used in 220 cc Banbury mixer. In order to minimize the oxidative thermal degradation, a nitrogen air flow was maintained in the mixing bowl. The products were collected as clumps with the help of a brass scraper. The materials were then compression molded by a hydraulic press for further characterization and analysis.

The commercial scale nanocomposites were prepared using a Leistritz, co-rotating twinscrew extruder (diameter =27 mm, L/D = 48) with a screw speed of 180 rpm and barrel temperature of 180°C for masterbatch and 200C and 200 rpm for letdown. The material was pelletized by a pelletizer BT 25 from Scheer Bay, Inc.

2.4 X-ray Diffraction

The X-ray diffraction (XRD) was used for characterization of crystal structure for different weight of silane treated nanoclay and polypropylene/clay nanocomposites. The technique was based on the fact that the atoms in crystals were arrayed in repeated units, and they serve as diffraction sites when exposed to X-ray beam. The wavelength of the X-ray beam and the incident angle of the X-ray beam follows Bragg's law:

$$n\lambda = 2dsin\theta \tag{2.1}$$

where *n* is the order of reflection, λ is the wavelength of the X-ray beam, *d* is the spacing between diffracting planes, and θ is the incident angle. Here only the first order of reflection is considered.

The *d*-spacing for montmorillonite (001) a basal plane is 0.95 nm. The organic treatment by various alkyl ammonium together with silane coupling agents can help organic molecules intercalated between inter planes of the clay, thus leading to an expansion of *d*-spacing. This shows on the XRD pattern as the peak shifts to the left with a lower 2ϑ corresponding to a greater distance between the inter planes.

A Bruker Davinci diffractometer at 40 kV and 40 mA with Ni-filtered Cu K_{α} radiation source was used in this study to characterize the *d*-spacing of inter planes of the organoclay. 1.2 mm slit was selected and mounted on the X-ray beam source side based on the resolution and intensity of the peak of interest. The test was performed over a 2 θ range of 0.1-10° with an increment of 0.02°.

2.5 Compression Molding

A Wabash hydraulic press was used to prepare samples for both shear rheology tests and extensional rheology tests. A 1.5 mm thick, 75 mm by 75 mm wide square mold was used to

prepare samples for shear rheology tests. Polymer pellets or chunks were placed in the mold, sandwiched by two polyimide release films on each side and this was placed between two thick steel plates. This mold assembly was placed in the center between the top and the bottom platen preheated at 200°C. After a proper amount time of heating, the mold assembly was compression molded at 1 ton for 1 min and then 8 tons for 5 mins, then cooled with circulating water at 8 tons for 12 min. A 4 rows by 5 columns rectangular molds on one piece of metal sheet was used for preparing samples for extensional rheology tests; each mold is 0.6 mm thick, 23.5 mm in length and 9.5 mm in width. The compression molding method for preparing samples for extensional rheology tests was similar to the previous method except that the compression force was 5 tons and the cooling time was 10 mins. The samples removed from the mold with care and were examined for defects, such as voids, cracks, foreign particles, etc.

2.6 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a thermo-analytical technique to monitor the difference in the heat flow rate to the sample and a reference sample as temperature is changing controlled by a program. The samples were held in a hermetically sealed aluminum pan. When the sample undergoes physical or chemical transformation under an enthalpy change, the instrument varies the heat flow provided to the sample to maintain the temperature unchanged in both sample holder and the reference holder. It can be used to characterize the melting temperature (T_m), crystallization temperature (T_c), the rate of crystallization and the crystallinity of the sample.

The polypropylenes, TPOs, and chemical blowing agents samples (5-10 mg) were tested using TA instrument Q10 under nitrogen purge of 50 ml/min with a ramp rate of 5°C/min or 10° C/min with a heat-cool-heat cycle or heat cycle only depending on the interest. The temperature

ranges from room temperature to 200 °C for the heating cycle and from 200°C to 50°C for the cooling cycle. The crystallinity of a given sample was determined following the equation:

$$\chi = \frac{\Delta H_f}{\Delta H_f^0 w_p} \tag{2.2}$$

Where ΔH_f is the second heating process heat of fusion for the composites, ΔH_f^0 is 207 J/g for polypropylene. w_p is polymer weight fraction.

2.7 Thermogravimetric analysis

The thermogravimetric analysis is a technique to monitor the weight loss as a function of temperature under controlled atmosphere. The weight loss at high temperature implies the burnt organic components in either TPO or organoclay. Thus the TGA analysis indicates the components change in the sample as temperature increasing.

For TPO and different amount of silane treated organoclay (10 mg), the TGA analysis was carried out on a TA instrument Q500 instrument with a temperature range from room temperature to 800°C at a high resolution ramp rate under nitrogen atmosphere. The high resolution ramp rate varies the heating/cooling rate of the furnace in response to changes in the rate of weight loss of the sample to improve the weight change resolution.

2.8 Rheology

Rheology is the science of materials deformation and flow under applied stress ^[113]. It has been used to study the relationship of the property-structure of the polymer melts or polymerparticle suspensions. In this study, the shear and extensional rheological properties of polypropylene/clay nanocomposites, and thermoplastic polyolefin/clay nanocomposites have been investigated.

2.8.1 Shear Rheology

Linear viscoelastic behavior of polymer is the change of stress behavior as the applied strain is small and was characterized by oscillatory shear tests. Parallel plates were used as the fixtures where the material is tested between a fixed bottom plate and a rotational top plate. As the top plate exerts a sinusoidal strain to the polymer melt sample, the corresponding axial stress is monitored by a pressure transducer connected to the top plate shaft. The oscillatory strain γ is and stress τ follow eqn. (3):

$$\gamma(t) = \gamma_0 \sin(\omega t) \tag{2.3}$$

$$\tau(t) = \tau_0 \sin(\omega t + \delta) \tag{2.4}$$

 ω is the frequency of the sinusoid, δ is the phase shift and usually called loss angle, and γ_0 and τ_0 is the strain amplitude and the stress amplitude, respectively.

The dynamic shear test results are usually reported using storage modulus G' and loss modulus G'' as eqn. (4) shown:

$$\tau(t) = \gamma_0 [G' \sin(\omega t) + G'' \cos(\omega t)]$$
(2.5)

The storage modulus G' and loss modulus G'' are calculated in terms of the amplitude ratio $G_d \equiv \frac{\tau_0}{\gamma_0}$

$$G' = G_d \cos(\delta) \tag{2.6}$$

$$G'' = G_d \sin(\delta) \tag{2.7}$$

The dynamic shear tests were carried out on a TA instrument ARES rheometer for polypropylene/clay and TPO/clay nanocomposites with 25 mm diameter parallel plates at selected

temperatures from 0.05 to 100 rad/s under continuous nitrogen atmosphere. The strain was selected at 2% for the nanocomposites and 4% for neat PP based on strain sweep tests at fixed frequency.

2.8.2 Extensional Rheology

Extensional rheology is important in a lot of polymer processing, such as thermoforming, film blowing, etc. During the foaming process, the cell wall during bubble growth process is mainly dominated by the extensional rheology. The extensional rheology is important to show the nonlinear behavior of the polymer in extensional deformation that cannot be represented by shear data. This is because the polymer chain is not fully stretched during shear tests.

In the current study, the melt strength of the polymer melt is quantified using extensional viscosity. Uniaxial extension is applied to a rectangular specimen with stretching along the longest dimension and compression in the other two directions. The melt extensional viscosity of the polymer nanocomposites was measured using an extensional viscosity fixture (EVF) fixture on a TA instruments ARES rheometer -- see Figure 2.3. The fixture consists of two cylinders or drums -- a fixed drum rotating around its axis, and the other orbiting around the fixed drum while rotating among its axis simultaneously. The force measuring cylinder is fixed and it can be coupled to the torque transducer of the TA instruments ARES rheometer.



Figure 2.3 The schematic of the extensional viscosity fixture.

The force $F_s(s)$ and area of the sample $A_s(t)$ (cross section area perpendicular to the stretching direction) are measured to calculate the extensional stress:

$$\sigma_E(t) = \frac{F_s(t)}{A_s(t)} \tag{2.8}$$

The transient extensional viscosity η_E is then calculated by:

$$\eta_E = \frac{\sigma_E(t)}{\frac{d}{dt}\varepsilon_H}$$
(2.9)

where ε_H is the Hencky strain and $\frac{d}{dt}\varepsilon_H$ is the Hencky strain rate. The extensional viscosity measurements were made for nanocomposites at 180°C for PP and PP nanocomposites and 200°C or 204°C for TPO and TPO nanocomposites and four strain rates 0.1, 0.5, 1 and 2 s⁻¹ over a Hencky strain of 3. The selected temperatures are well above the melting temperature of PP and TPO. Test

specimens (24 mm \times 10 mm \times 0.75 mm) were compression molded under 5 tons for 5 min. The specimens free of voids or defects were selected as the testing specimens and checked for sagging due to gravity effect during after loading and during delay time before test. After each test, the specimen was also checked to ensure uniform stretching in the middle portion of the sample.

2.9 Foaming Procedure

Injection molding foaming process with a core-back command module added was used for foaming (see Figure 1.1). Here the chemical blowing agent was used. The pellet form polymer specimens dry-mixed with a chemical foaming agent were fed into the hopper to the preheated extruder. When a set amount of (shot size) the melt with dissolved CFA accumulated in the screw before entering the manifold, the screw in the extruder will retract, and extrusion back pressure will be exerted to balance the retraction preventing the bubbles from early expansion. After a filling stage (melt filled the mold), and a short packing stage (a pack pressure will be provided in the mold), one side of the mold will be precisely opened to a position and increase the mold cavity rapidly. Meanwhile, the pressure from the packing stage will be released quickly leading to a rapid bubble growth. The injection time was adjusted to be around 1 s when adjusting the injection speed. A FANUC S-2000i275B injection molding machine with a core-back tool add-on was used.

The foam plaques were prepared a mold with the dimension 420 mm by 150 mm with the thickness dimension starting from 1.75 mm and after the core-back stage, the thickness was expanded to 2.8 mm. The temperature profile varied between different materials, and the manifold temperature was 202°C or 213°C, extrusion back pressure varied between 400 and 1500 psi, injection speed was 63.5 mm/s or 76.3 mm/s the extrusion rate was 50 rpm, pack pressure varied from 6.9 MPa to 34.4 MPa and the pack time was 1 s, and the mold temperature was kept at 49°C and mold opening speed kept at 250.4 mm/s.

The specimens for tensile and flexural tests were prepared using a tensile bar mold with both 3 mm and 4 mm thick tensile bar geometries on the same injection molding machine. The tensile bar is 150 mm long by 10 mm wide and the MD-TD plane of the 3 mm tensile bar was perpendicular to the mold opening direction and 4 mm tensile bar was parallel to the mold opening direction. The core-back stage expanded the 3 mm tensile bar foam to 4 mm. The solid tensile bars were molded by the same tensile bar mold with the 4 mm thick specimen without the core-back stage. The molding conditions for ADX and ADXNB4 using 2 wt% ADX 1099 CFA were the same. The temperature profile from nozzle to rear was set at 204-204-207-196-185-49°C, and the manifold temperature was 202°C. The extrusion rate was 50 rpm and the extrusion back pressure was 5.5 MPa. The pack pressure was kept at 31 MPa for 1s packing time with injection speed at 33 mm/s and the mold opening speed 250.4 mm/s.

2.10 Characterization of Die-Drawn Product and Foam

2.10.1 Density Measurement

The density of the die-drawn specimen and foam was characterized using a Sartorius YDK 01 density kit based on the Archimede's principle. The solid immersed in the liquid is subjected to the force of buoyancy. The buoyancy force is equal to the weight of the volume of the liquid that the sample displaced. Water was used as the liquid and with a hydrostatic balance, the weight of the sample in the air W(a) and in the water can be monitored W(l), and the sample can be measured using the eqn. 2.10:

$$\rho = \frac{W(a) * \rho(l)}{W(a) - W(l)}$$
(2.10)

At least three measurements were performed for each die-drawn or foam specimen in order to attain the average value as the final result.

2.10.2 Scanning Electron Microscopy

Scanning electron microscope (SEM) is used for detecting topological information of the surface of a sample by scanning with a focused beam of electrons. Under high vacuum, the primary electrons emitted either from heated tungsten or a filament in a huge electrical potential (Field emission SEM) bombast on the surface of the sample, the secondary electrons from atoms on the surface of the samples will be emitted and detected by a detector, converted to a voltage and then amplified. The amplified voltage will then be applied to the grid of cathode-ray tube (CRT) and the intensity of the spot of light on the surface varies as the topology changes. When the beam is on a projection on the surface, the detector will collect a greater number of secondary electrons leading to a higher voltage, showing as a bright spot on the surface CRT; As contrary, when the beam is on a depression on the sample surface, fewer secondary electrons will be collected resulting in a smaller voltage and a dark spot on the surface of CRT. The SEM image is composed of thousands of spots with varied intensity on the CRT surface.

As opposed to that the secondary electrons are from the surface atoms knocked out by the beam electrons, the backscattered electrons are the beam electrons after elastic interaction or back scattered by the sample to a certain escape depth. Thus the backscattered electron image does not reflect the surface morphology but the image of some depth below the sample. Usually the backscattered electrons have a much higher energy than the secondary electrons and need a separate backscattered detector compared to secondary electron detector. The percentage of beam electrons scattered is increasing as the atom molecular weight increasing. Thus the regions with lower molecular weight atoms.

Scanning electronic micrographs (SEM) and backscattered electron micrographs (BEI) were obtained using JEOL 6610LV SEM. For die drawing sample MD-TD surface and no special treatment was done before coating. For MD-ND samples, they were scored on the top surface of the desired MD-ND plane, immersed in liquid nitrogen for 30 min, fractured, and coated with platinum or gold on the fractured surface. The fracture plane for injection molded foam plaques is illustrated by Figure 2.4. The cell size distribution and the mean diameter of cells were analyzed using Image J software. The cell density *N* was calculated using the equation 2.11:

$$N = \left(\frac{n}{A}\right)^{1.5} \tag{2.11}$$

Where *n* is the number of cells in the defined area *A*, derived from SEM micrographs.



Figure 2.4 Injection molded foam schematic for SEM sample location.

2.10.3 Transmission Electron Microscopy

Transmission electron microscopes (TEM) are microscopes with electrons transmitted through a less than 100 nm thin film of the specimen analogous to light optical microscope. Compared to optical microscope, the TEM resolution can be as small as 0.01 nm due to the small wavelength of electrons. Under high vacuum, an image is formed when the electron beam transmitted and interacted with the sample, and then magnified and focused on an imaging device. The dark region on TEM image is usually where the samples are thick with large molecular weight of atoms. The light region on TEM image are thin regions with small molecular weight of atoms. In the case of PP/clay nanocomposites, the dispersed clay layers show up as the dark fine in light PP region. In the case of TPO/clay nanocomposites, the dark fine lines are clay while the dark thick lines are talc, and the lightest region is PP and the grey shade represents the rubber phase. TEM has been used for quantifying exfoliation of nanoparticles but is limited in the area detected may not represent the dispersion in the nanocomposites.

The specimen for the TEM imaging was prepared using ultra-microtoming method for this study by a PTXL ultra-microtome (RMC, Boeckeler Instruments) connected to a CRX cryo unit. The compression molded disc was cut in to a small rectangular piece and then mounted to the ultra-microtome. A 90 nm thick section of the sample was prepared by ultra-microtoming in liquid nitrogen at -120°C and collected on a 200 mesh copper grid, following by a staining procedure by ruthenium tetroxide up to 6 hours before imaging. In this study, the TEM images were taken by a JEOL100 CXII equipment with an accelerating voltage of 100 kV.

2.10.4 Mechanical Properties

Tensile test

For injection molded tensile bars, the specimen was 150 mm long by 19 mm wide and 4 mm thick. Tensile tests were performed on an Instron 5982 with 1000 N load cell at testing speed of 5.04 mm/min. For die-drawn products, the tensile tests were performed using a United Testing Systems model STM-20 tensile test frame with 88964 N load cell. The tensile bar specimen was clamped between two grips and the testing speed was using 5.04 mm/min controlled by a template set up in advance in Datum 5.0 software by United Testing Systems. For die-drawn samples, the ASTM D638 was used. Tensile test specimens (dog-bone shaped) were cut out from the billets before drawing directly with the help of a cutter. Several tensile specimens were cut from the dirawn billets at different locations: 9.9, 25.1, 45.4, 75.9 and 106.4 cm from the die exit. These

specimens were 14 cm long with a gage length of 6.35 cm and were cut with the cutter placed in a Carver laboratory press and a force of 19.6 kN.

Puncture test

Puncture penetration tests were conducted to investigate the separator resistance against a sharp probe following ASTM F1306-90. The puncture test specimens were cut into 27 mm by 27 mm squares with the thickness measured by a micrometer. The specimen was placed in the center of the clamp with MD parallel to the width of the plate between two identical plates. The puncture resistance testing followed ASTM F1306-90 with a penetration rate of 25.4 mm/min.

Chapter 3. Effect of Different Extent of Silylation on Dispersion of Clay in Polypropylene Nanocomposites

3.1 Introduction

Compared to traditional inorganic fillers for polymer matrix, nanoclay has attracted extensive attention in various fields due to the light weight, high aspect ratio, high surface area and adsorption properties. One of the applications is to improve the tensile modulus and strength of the polymer matrix^[112]. Studies have also reported that the addition of clay can greatly increase cell density, reduce cell size and improve uniformity of cell size for linear PP foam^[6, 12, 114]. The desired properties require good dispersion of the hydrophilic nanoclay in the hydrophobic polymer. Chemical modification is one way to improve the polymer-particle interaction. For example, the sodium montmorillonite can be modified by exchanging the sodium ions by alkylammonium ions, and this process can expand the distance of the interlayer, or *d*-spacing of the clay. The dispersion of clay is also greatly improved when compounded with a maleic anhydride grafted polypropylene compatibilizer up to 25 wt%^[37]. However, the PP-g-MA usually is low viscosity and is harmful to the mechanical property of the nanocomposites.

Two different types of sites on the organoclay can be hydrogen bonded to PP-g-MA: one is hydroxyl group on the edge of the organoclay and the other is the oxygen group on the faces of the organoclay ^[44]. People have demonstrated that depending on the structure of the silane coupling agent could either enter the gallery or react with the edge hydroxyl groups^[10, 44]. The silane grafting reaction can happen either in a solvent base (wet process) or from the silane vapor saturation (dry process) at the boiling point of the silane coupling agents. The grafting reaction from the vapor saturation compared to solvent media favors the silane molecules entering the clay galleries, resulting in expansion of the interlayer spacing or *d*-spacing^[9, 10]. In wet process, the hydrolyzed silane molecules easily condense among themselves before entering the interlayer of organoclay and the bulky condensed siloxane is harder to enter the galleries even at a high level of silane coupling agent^[10]. Another reason is that the silane hydrolysis can happen in the interlayer of the clay and simultaneous condensation of the silane bonded to the adjacent layers can fix the gallery height of the clay^[48]. In vapor phase saturation process, a much lower level of silane is sufficient for basal spacing expansion because the hydrolysis and condensations happen after the single silane molecules enter the galleries^[9]. However, when the silane coupling agent level is too high, the excessive silane molecules could still condense among themselves and prevent the expansion of the clay galleries. Thus an optimized amount of silane coupling agent should be designed, which have not been reported before.

The objective of the current research is to compare the effect of different levels of vapor phase silane grafted montmorillonite and the dispersion in polypropylene system compatibilized with PP-g-MA. The *d*-spacing, thermal weight loss properties of the silylated clay and the rheology and morphology of the PP nanocomposites with silylated clay were examined.

3.2 Experimental Details

3.2.1 Materials and Procedures

The details of nanocomposites prepared for this study have been presented in Table 3.1. Profax 6523 (Dow Chemical, Co.) has a melting temperature of 168 °C. Exxelor PO1015 (from Exxon Mobile Co.) is maleic anhydride grafted polypropylene (PP-g-MA) served as the compatibilizer. The organically modified montmorillonite I.44P clay (from Nanocor, Inc.) was grafted under saturated vapor from aminopropyl dimethoxysilane (Dynasylan 1411 from Evonik, Inc.) by Malvern Co around 254-271°C, which is the boiling point of this silane coupling agent at 101300 Pa.

	Polymer matrix	Amount of silane treated I.44P clay	Amount of clay (wt%)	Masterbatch component PP-g-MA (PO1015) to clay ratio
PPNC5	Profax 6523	0.5 wt%	5	1:1
PPNC8	Profax 6523	0.8 wt%	5	1:1
PPNC10	Profax 6523	1.0 wt%	5	1:1

 Table 3.1 The components of PP/clay nanocomposites.

3.2.2 Processing and Characterization

The silane grafted I.44P montmorillonite was sieved using a no. 200 sieve. Then the PP-g-MA and the silane grafted I.44P organoclays were dried at 80°C with a vacuum of 500 mmHg for 12 hrs to remove the water moisture. A masterbatch made of PP-g-MA and organoclay 1:1 ratio was made first using a Brabender batch mixer at 180°C and 150 rpm for 8 min with continuous nitrogen purge. Then the masterbatch was letdown to 5 wt% clay at the same temperature and rotary speed for 10 min.

The 0, 0.5, 0.8, 1.0 and 1.5 wt% silane treated clay was dried at 80°C with a vacuum of 500 mmHg for 12 hrs before X-ray diffraction (XRD), thermogravimetric analysis (TGA) characterization. XRD was used to characterize the distance of the interlayer of the stacked clay platelets using Bruker Davinci diffractometer operating at 40 kV, 40 mA with Ni-filtered Cu K_{α} radiation source. TGA was carried out with a TA instruments Q500 apparatus to evaluate the weight loss of various organoclays with increasing temperature. The analysis was performed by heating 10 mg of organoclay powder from room temperature to 800°C using a 4°C/min high resolution ramp under the nitrogen atmosphere. Dynamic shear tests were carried out on a TA instruments ARES rheometer with 25 mm parallel plates. Compression molded disc specimens were tested over a frequency range of 0.05-100 rad/s at 4% strain for PP6523 and 2% strain for nanocomposites under nitrogen atmosphere. The melt extensional viscosity of the nanocomposites

was measured using an extensional viscosity fixture (EVF) on a TA instruments ARES rheometer under nitrogen atmosphere. Test specimens (24 mm × 10 mm × 0.75 mm) for were prepared by compression molding under and 5 tons for 5 min at 200°C. The extensional viscosity measurements were performed at 180°C and four strain rates 0.1, 0.5, 1 and 2 s⁻¹ over Hencky strains up to 3. The TEM micrographs of various nanocomposites were obtained with a JEOL100 CXII instrument at 100 kV accelerating voltage. TEM samples were prepared by microtoming of 1.5 mm thick compression molded discs into 90 nm thick samples using PTXL ultra-microtome (RMC, Boeckeler Instruments) connected to a CRX cryo unit and collected on a 200 mesh copper grid.

3.3 Results and Discussion

3.3.1 Characterization of clay and polymer nanocomposites

The X-ray diffraction patterns of 0, 0.5, 0.8, 1.0 and 1.5 wt% silane treated I.44P clay were detected and have been plotted in Figure 3.1. The *d*-spacing of no silane grafted I.44P clay was the smallest, corresponding to the peak location right most. Among the silane treated clays, 0.8 wt% silane treated clay has the greatest *d*-spacing with the peak shifted to the left most among the four X-ray diffraction patterns. This indicates that the amount of silane molecules reacted at the faces of the nanolayers is the greatest for in 0.8 wt% silane treated clay, with the most significant expansion of the galleries at this silane treatment level.



Figure 3.1 XRD patterns of the three levels of silane coupling agent treated clay.

The X-ray diffraction patterns of the PP nanocomposites mixed with different level of silane treated organoclays were also characterized and have been presented in Figure 3.2.



Figure 3.2 XRD patterns of three PPNCs compared to the three levels of silane coupling agent treated clay.

In general, the *d*-spacing is increased from clay to PPNC for all the cases and the curves of the PPNC have less prominent peak compared to silane treated clays; this is due to the intercalation of maleic anhydride group to the interlayer of the clay: the maleic anhydride group reacts to the amine group on aminopropyl dimethoxysilane, and the latter forms either a hydrogen bond to the oxygen group on the face or a covalent bond to the hydroxyl group on the edge of the clay ^[44]. Even though PPNC5 and PPNC8 has the similar *d*-spacing, the d (001) peak is flatter for PPNC8, which indicates better exfoliation of clay in PPNC8 compared to PPNC5 as a sharp peak indicates the d(001) peak of the parallel clay galleries. The dispersion of clay in PPNC5, PPNC8 and PPNC10 were examined using transmission electron microscope- see Figure 3.3 (20000× magnification) and 3.4 (40000× magnification). The black lines indicate clay while the background represents PP and PP-g-MA matrix.





Figure 3.3 (cont'd)



50



Figure 3.4 The TEM of (a) PPNC5 (b) PPNC8 and (c) PPNC10 magnification 40000×.



It was observed that a great number of finer dark lines representing more exfoliated clay in the TEM of PPNC8 compared to the other two nanocomposites in both Figure 3.4 and 3.5. This means that the dispersion of clay is the best in PPNC8 with the 0.8 wt% silane treated clay, which is consistent with the flattest X-ray diffraction peak representing more exfoliation for PPNC8. Thus the 0.8 wt% silane treated clay was proved to have the largest *d*-spacing and the greatest dispersion in the PPNC.

3.3.2 Rheology characterization

The frequency-dependent dynamic shear storage modulus and dynamic viscosity for PPNC5, PPNC8 and PPNC10 have been plotted in Figure 3.5 and Figure 3.6, respectively. As expected, the PPNCs have a higher shear modulus and shear viscosity compared to PP matrix especially at low frequencies. For storage modulus frequency sweep curves, the frequency did not start low enough to signify the plateau in the beginning portion though. The curves for shear modulus and shear viscosity frequency sweep for PPNC5, PPNC8 and PPNC10 are similar to each other.



Figure 3.5 Storage modulus of PP and PPNCs.





The uniaxial extensional viscosity transients at four strain rates ranging from 0.1 s⁻¹ to 2.0 s⁻¹ have been plotted for the three nanocomposite melts in Figure 3.7. The extent of strain hardening was quantified by a strain hardening ratio χ between the actual value of extensional viscosity and the value of calculated extensional viscosity based on the base line. The base line or linear viscoelastic "envelope" was fitted by extrapolating the data from 0.1 to 0.4 s for 0.1s⁻¹ curves. The maximum strain hardening ratios χ_{max} are evaluated at the highest strain before the stretched specimens break or deformed nonuniformly. This corresponds to a strain ratio of 1.5 for three nanocomposite melts and the maximum strain hardening ratio is the largest for PPNC8 melt compared to other two nanocomposite melts at 0.5 s⁻¹ and 1 s⁻¹ strain rates and the same as PPNC5 at 2 s⁻¹ strain rate.



Figure 3.7 Uniaxial extensional viscosity transients (η^*_{e}) at several strain rates for compounded nanocomposite melts.



Figure 3.8 Maximum strain hardening ratio of PPNC5, PPNC8 and PPNC10 at 180°C; this corresponds at all strain rates to a strain of 1.5.

3.3.3 Characterization of the residual clumps of sieved clay

The images of residual clumps from sieving of 50 g of clay treated with 0.5, 0.8 and 1.5 wt% of the silane coupling agent have been presented in Figure 3.9.



Figure 3.9 The image of clumps after sieving (a) 0.5 wt% (b) 0.8 wt% and (c) 1.5 wt% silane treated clay.



The smallest and most uniform clumps was observed for 0.8 wt% silane treated clay compared to 0.5 wt% and 1.5 wt% silane treated clay. The most amount of the clumps was found for 1.5 wt% silane treated clay. The measured weight fraction of the clumps in 50 g of clay was measured and summarized in Table 3.2.

Table 3.2 The weight fraction of clumps in the clay

The amount of silane treated clay, wt%	Weight of clumps, g	Weight Fraction
0.5	0.6	0.01
0.8	1.0	0.02
1.5	3.6	0.07

The weight of clumps was the greatest for 1.5 wt% silane treated clay, which was consistent with the images of the clumps in Figure 3.9. The clumps could be condensed silanol polymer or aggregated clays due to surfactant loss. The PPNC 10 shows more clumps compared to PPNC5 and PPNC8, which means that more surface is lost leading to a lower *d*-spacing of clay and is consistent with the XRD results in previous section.

3.4 Conclusion

The organoclays after vapor phase silane treatment at 0.5, 0.8, 1, and 1.5 wt% silane level and their nanocomposites with PP and PP-g-MA compatiblizer were characterized. The XRD result shows the greatest interlayer spacing for 0.8 wt% silylated clay, as well as the greatest exfoliation of the same clay in PP nanocomposites, leading to the most dispersed morphology from by TEM characterization. The same nanocomposite shows the greatest strain hardening degree from rheology tests among all PP nanocomposites. This is due to that both the surfactant loss and condensed siloxane polymer under high temperature is the least with the smallest and most uniform of clumps representing both aggregated clay clusters and the condensed siloxane polymer after sieving the silylated clay at 0.8 wt% silane level.

Chapter 4. Melt rheology, Surface Appearance, Morphology and Mechanical Properties of Core-back Injection Molded TPO Foams with Talc and Clay

Additives

4.1 Introduction

With the increasing need to reduce energy consumption and pollution, lighter and thinner injection molded parts with less density can decrease the material and reduce the energy consumption with the desired mechanical properties. Compared to batch foaming and extrusion foaming, foam injection molding (FIM) has attracted much attention to researchers because its ability to produce parts in varied shapes in short production cycles.

The FIM can be divided into low pressure FIM or high pressure FIM based on the pressure inside the mold^[19]. In low pressure FIM, the shot size is less than the cavity (short shot) and the bubble nucleation and growth occur once entering the mold due to the lower pressure in the mold compared to the pressure inside the bubbles. As the filling goes on, the bubble size is greater near the end of fill position compared to the position near the gate due to the reduced pressure drop rate when filling the mold cavity. Even though the bubbles are non-uniform, up to 40% void fraction of the foam parts can be attained^[19]. High pressure FIM is full-shot injection and the bubbles nucleation occurs as the flow of polymer melt enters the mold, but the high pressure provided in the mold or pack pressure during the packing stage will redissolve "gate-nucleated bubbles" in the melt. Then bubble nucleation and expansion driving force is dominated by the shrinkage of polymer melt during solidification process^[18]. Thus the cell size is more uniform in high FIM, but the void fraction is restricted to be 5% -10%^[19].

One side of mold wall opening or core-back step right after packing stage is applied to produce a more uniform cell structure with greater void fraction in the parts compared to the conventional FIM. After a packing stage where the nucleation of bubbles can be redissolved in the polymer melt just as in the high FIM, one side of the mold is opened precisely to a pre-defined position at a set mold-opening speed. The expansion of foams is along the mold-opening direction, typically in the thickness direction of the molded part, and the pressure drop rate is controlled by the mold-opening speed. The foam density can be controlled by the mold opening distance and a higher cell density with finer cell size can be attained as the mold-opening speed increases^[19, 115].

TPO has been widely applied to the automotive industry as both exterior such as bumper fascia and interior materials like dashboard, door panels, etc. It is composed of a continuous PP phase embedded with elastomeric phase such as ethylene-co-octene or ethylene-propylene rubber phase (EPR) with greater abrasion resistance, toughness and flexural properties due to the rubber phase. Previous study has reported that a low melt temperature contributes to a small cell size in both physical and chemical foaming of TPO ^[20, 57].

The unfilled TPO tends to shrink and contain surface defects. One type of the defects is flow marks or "tiger stripes" on the surface of the molded parts due to the rapid retraction of the rubber phase^[56]. The jetting and silver streaks on the surface of the molded FIM of TPO plaques were another type of defects^[57]. Talc fillers were reported to have a better effect on improving the surface appearance of the FIM molded parts compared to organoclay or silica for FIM of TPO^[58]. The commercial TPO typically contains talc particles around 20 wt% to reduce the shrinkage and attain smooth surface. Also, the talc particles could create more heterogenous nucleation sites on the surface. Yetkin *et al.* ^[54] reduced the mean pore diameter from 360-550 micron to 175-235 with 20 wt% talc loading for conventional FIM using CFAs. Santoni *et al.* ^[4] attained a greater cell
density with smaller cell size of the FIM of TPO with the addition of 10 wt% talc loading and PPg-MA. Not many studies were reported for FIM of TPO and clay nanocomposites. Hwang et al. ^[55] studied clay filled LDPE with EPR nanocomposites which showed shear thinning behavior for the nanocomposite melt, with varied clay loading from 1 to 7 wt% and only 1 wt% maleic anhydride modified PP (PP-g-MA) and attained reduced cell size from 105 micron to 75 micron with 7 wt% clay loading using Mucell ® technology. However, there is no clear relationship of the shear thinning behavior and the foamability of the material and uniformity of the cells. Also, not enough attention was paid to the dispersion of the clay and the location of the clay in TPO before foaming process. Studies on TPO/clay nanocomposites without addition of PP-g-MA^[50] reported that the clay particles tend to be aggregated on the elastomer phase. By using different compatibilizer, the clay could be either intercalated tactoids in elastomer phase using maleic anhydride modified elastomer^[50, 116], or exfoliated at the interface of the PP and rubber phase using PP-g-MA^[5, 51]. The toughness property was opposite for these two types of TPO/clay nanocomposites- a greater toughness was observed for the TPO with clay in the elastomer phase while lower toughness was observed for TPO with clay on the interface^[51, 116]. In the current study, to make the most of the surface area of the clay to be nucleation sites, the clay should be dispersed in PP phase, which requires enough PP-g-MA to disperse the clay to migrate to PP phase. However, the PP-g-MA usually has a much lower viscosity compared to the PP, and the mechanical property, especially elongation is lowered. Tiwari *et al.* ^[51] have reported that the addition of 3 wt% clay with 1.5:1 ratio PP-g-MA to clay reduced the elongation at break of the TPO/clay nanocomposites by half. Therefore, a lower usage of PP-g-MA to maintain good dispersion of clay is crucial.

Previous work in our group has proved that pretreating organoclay with silane coupling agent in solvent leads to significant reduction in cell size, and increase in cell density for foam extruded TPO/ silylated clay nanocomposites, and the vapor phase silane treatment from Chapter 3 expands the interlayer of clay even better compared to wet process and 0.8 wt% silane treated clay provides with the greatest exfoliation of clay in linear PP with PP-g-MA to clay ratio 1:1.

The objective of this research is to understand the relationship between melt rheology, surface appearance, foam morphology and mechanical properties of foam injection molded talc filled TPO and organoclay additive with optimized level of vapor phase silane pretreatment. The core-back FIM with chemical foaming agent will be adopted to generate structural foams of two different geometries whose structure will be detected by SEM. A plaque mold will be used to study the surface appearance of the foamed plaques and a tensile bar mold for specimens for mechanical tests.

4.2 Materials and Procedure

4.2.1 Materials

The details of nanocomposites compounds made from TPO grade ADX 5349 for this study have been presented in Table 4.1. One melting peak was noted for ADX 5349 (Advanced Composites, Inc.) in differential scanning calorimetry (DSC) measurement at 166°C. Thermalgravimetric analysis (TA instruments Q500) and Fourier transform infrared spectroscopy results indicate that 23 wt% talc fillers were also included in the ADX 5349. Two different maleic anhydride grafted polypropylene (PP-g-MA) acted as the compatibilizer were used: Exxelor PO1015 (from Exxon Mobile Co.) and Bondyram 1001 (from Polyram, Ltd.). The melting flow index is 150 g/10 min for PO1015 and 96 g/10 min for Bondyram 1001. The maleic anhydride content is 0.5 wt% for PO1015 using PP copolymer and 0.95 wt% for Bondyram 1001 using PP homopolymer. The I.44P montmorillonite clay (from Nanocor, Inc.) was grafted under saturated vapor of aminopropyl dimethoxysilane (Dynasylan 1411 from Evonik, Inc.) by Malvern Co. 0.8 wt% silane treatment on I.44P clay was picked leading to the largest *d*-spacing and greatest dispersion of clay in PP matrix according to previous work (Chapter 3). ADX 1099 CFA (Advanced Composites, Inc.) and SAFOAM CE335 (Reedy Chemical Foam & Specialty Additives) are both endothermic foaming agents with gas evolution of 33 ml/g and 50 ml/gram.

Compound	Silated clay	PP-g-MA grade	Third component in masterbatch	Composition of masterbatch (wt. fractions)
ADXNC1	3 wt%	PO1015	PP6523	0.267,0.533,0.2
ADXNC2	3.5 wt%	PO1015	ADX 5349	0.267,0.533,0.2
ADXNB4	3.5 wt%	Bondyram 1001	ADX 5349	0.229,0.571,0.2

Table 4.1 Composition of molding compounds by extrusion based on the TPO grade ADX 5349

4.2.2 Procedure

The ADXNC2 and ADXNB4 compounds were prepared using a Leistritz, co-rotating twinscrew extruder (diameter =27 mm, L/D = 48) at 180°C and 180 rpm for masterbatch (the components of masterbatch are listed in Table 4.1 and 200°C and 200 rpm for letdown.

The pellet form compound listed in Table 4.1 was dry-mixed with 2% ADX1099 CFA pellet and injection molding foamed using FANUC S-2000i275B injection molding machine during a core-back process. The injection molding conditions listed in Table 4.2 and the temperature was selected based on the shear viscosity measurements in the next section. The injection molded foam plaque was 420 mm long and 150 mm wide, and the thickness increased from 1.75 mm to 2.75 mm after foaming during core-back process.

Compound	RPM	Injection speed mm/s	Zone temperature from nozzle to rear °C (Manifold temp °C)	Extrusion back pressure MPa	Shot size mm	Pack pressure MPa/s
ADX	60	76.2	199-210-199-191-182-49 (202)	5.5	66.4	6.9/1
ADXNC2	50	63.5	216-218-218-216-207-49 (213)	5.5	68.3	20.7/1
ADXNB4	50	63.5	204-204-207-196-185-49 (202)	5.5	63.5	34.5/1

Table 4.2 Molding conditions of ADX, ADXNC2 and ADXNB4 foam plaques

The melt extensional viscosity of TPO and TPO nanocomposites was characterized using an extensional viscosity fixture (EVF) on a TA instruments ARES rheometer for samples at 200°C and 204°C and three strain rates (0.5, 1, $2s^{-1}$). Test specimens (24 mm by 10 mm by 0.75 mm) were compression molded at 180°C and 5 tons for 5 min. The shear viscosity for TPO and TPO nanocomposites was measured at six shear rates (180.2, 540.5, 900.8, 1261.2, 1621.5 and 2017.9 s⁻¹) using a Dynisco LCR6000 capillary rheometer with a capillary die of 1.5 mm and L/D=20.

Scanning electronic micrographs (SEM) were obtained using JEOL 6610LV instrument. The SEM specimens were scored on the top surface, immersed in liquid nitrogen for 30 min, fractured, and coated with platinum or gold on the fractured surface. The SEM specimens of foam plaques were taken from three locations from foam plaques to examine the TD-ND cross-sectionsee Figure 4.1. The SEM specimens of tensile bars were taken from 50 mm from the side close to the gate. The cell size distribution and mean cell size of the foam were analyzed using Image J software. The cell density was calculated following eqn. 2.11.

Transmission electron micrographs (TEM) were obtained with JEOL100 CXII instrument at 100 kV accelerating voltage, from 90 nm thick sections cryomicrotomed, collected on a 200 mesh copper grid and then stained by ruthenium tetroxide up to 6 hours before imaging. The cell density was calculated following eqn. 2.11.



Figure 4.1 The schematic of the foam plaque and SEM specimen locations.

The tensile tests were performed on an Instron 5982 instrument with 1000 N load cell at 5 mm/min according to ISO 527 standard. The 150 mm long by 10 mm wide by 3 mm or 4 mm molded tensile bar specimens were prepared using a designed tensile bar tool mold using the same injection molding machine as molding plaques with the following molding conditions for both ADX and ADXNB4 samples (Table 4.3). The flexural properties were characterized by International Automotive Group, Inc, using an Instron 4465C9257 instrument and ISO 178 standard at 2 mm/min. The specimens were made the same way as for tensile test samples.

Compound	RPM	Injection speed mm/s	Zone temperature from nozzle to rear °C (Manifold temp °C)	Extrusion back pressure MPa	Shot size mm	Pack pressure MPa/s
ADX & ADXNB4 tensile bar	50	33.0	204-204-207-196-185- 49 (202)	5.5	34.8	31.0/1

 Table 4.3 Molding conditions for ADX and ADXNB4 tensile bar

4.3 Results and discussion

4.3.1 Characterization of TPO and TPO nanocomposites

4.3.1.1 Morphology of the TPO and TPONC

The morphology of the ADX and ADXNC2 was examined by TEM and has been presented in Figure 4.2.



Figure 4.2 Transmission electron micrographs of (a) ADX 5349 magnification $6700 \times$ (b) ADXNC1 magnification $6700 \times$ (c) ADXNC2 magnification $10000 \times$ (d) ADXNB4 at different locations magnification $10000 \times$.

Figure 4.2 (Cont'd)



Figure 4.2 (Cont'd)



The lightest regions are voids due to microtoming procedure, and the second lightest continuous region represents the PP phase in all figures in Figure 4.2. The shaded areas stand for the rubber phase in the TPO from staining procedure by ruthenium tetroxide. The talc particles are typically 1.5 µm long and 0.2 µm thick represented as the darkest lines in Figure 4.2 (a). The clay particles are presented by the finer lines in Figure 4.2 (b) (c) and (d). The dimension of the rubber particles was decreased with the addition of clay, which is consistent with previous studies^[5, 50, 51, 116]. The clay particles were observed in both PP and rubber phase. Previous work has reported that when no PP-g-MA is added, the clay particles tend to aggregate in rubber phase, but with addition of PP-g-MA to TPO without talc particles, the clay particles could be dispersed mostly on the rubber and PP interface. However, in the current study, the talc particles may hinder the dispersion of the clay particles because the talc particles have similar sandwich structure as the clay with oxygen sites that could be hydrogen bonded to the PP-g-MA. This indicates that the PP-g-MA may attach

to the talc particles instead of clay to serve as compatibilizer for the talc particles. This explains why the PP-g-MA to clay ratio of 1:1 used in PP system in Chapter 3 was not enough to attain strain hardening behavior or good dispersion of the clay. Previous work reported that the addition of even 1% PP-g-MA could lead to a better dispersion of talc and greater cell density and smaller cell size for TPO FIM^[4]. However, in the current study, more aggregated talc particles were observed in the TPO nanocomposites compared to base TPO; this could be attributed to that the addition of the talc filled TPO in the masterbatch, as well as the letdown step irritated the dispersion of the talc particles. Thus less effective talc particles could serve as nucleation sites in the PP phase where bubbles are easier to grow with lower viscosity compared to the rubber phase, which will be discussed in the foam morphology section. The location of the talc particles is also crucial for the properties and a statistical analysis was performed for the area fraction of talc at different locations. The area fraction of the talc particles in PP region, interface of the PP and rubber phase, or in rubbers phase was analyzed and has been presented in Table 4.4.

	РР	PP and rubber interface	rubber
ADX	0.24	0.50	0.26
ADXNC1	0.23	0.19	0.59
ADXNC2	0.25	0.34	0.41
ADXNB4	0.19	0.17	0.64

Table 4.4 The area fraction of talc particles at different locations in composites

After compounding of ADX with PP-g-MA and organoclay, the volume fraction of talc in the PP and rubber interface decreased but more talc particles are in the rubber phase. This means that the dispersion of clay particles may cause migration of talc particles into the rubber phase.

4.3.1.2 Rheology of the TPO and TPONC

The uniaxial extensional viscosity transients at strain rates ranging from 0.5 s^{-1} to 2 s^{-1} have been plotted for nanocomposite melts ADX, ADXNC2 and ADXNB4 in Figure 4.3. Each of these runs was carried out under a maximum specified Hencky strain of 3.



Figure 4.3 Uniaxial extensional viscosity transients (η_E^+) at several strain rates for (a) ADX (b) ADXNC2 and (c) ADXNB4.

Figure 4.3 (Cont'd)



The strain hardening effect was not discovered in ADX melt in a uniaxial extensional flow but appeared in both ADXNC2 and ADXNB4 melt, showing elevated extensional viscosity at nonlinear region compared to the based curve or linear viscoelastic "envelope". This is a metric that the melt strength is strong enough to better control the cell structure. Bondyram 1001, a homopolymer PP-g-MA with lower MFI was used for ADXNB4 compared to PO1015- a propylene-ethylene copolymer PP-g-MA with higher MFI in ADXNC2. Even though the maleic anhydride content for PO1015 is half of that in Bondyram 1001, the PP-g-MA to clay ratio were increased to 2.5:1 to attain strain hardening behavior. This could be attributed to that the maleic anhydride group attached to homopolymer PP only at the end of the chains as opposed to sites at both the end and the middle of the chains in copolymer PP. Thus the interaction between the PP and the clay was not as strong in ADXNB4 compared to ADXNC2 when using the same amount of PP-g-MA. The shear viscosity of ADX, ADXNC2 and ADXNB4 were tested using both a parallel plate fixture on a rheometer and a capillary rheometer at 210°C and the results have been plotted in Figure 4.4 and 4.5, respectively.



Figure 4.4 Dynamic viscosity of TPO and TPO nanocomposites.



Figure 4.5 The shear viscosity of (a) ADXNC2 (b) ADXNB4 compared to ADX.

Figure 4.5 (Cont'd)



The dynamic shear viscosity for ADXNB4 deviated from ADX the greatest at low frequency from 0.1-100 rad/s but was close to ADX at high frequencies 100-2000s⁻¹. The dynamic shear viscosity of ADXNC2 deviated from the ADX the most around 200 s⁻¹ and was close only at a shear rate of 2000 s⁻¹. The shear viscosity characterized at greater frequencies in a capillary rheometer was closer to the shear rate of the composites melt in the mold. The shear rate for steady flow between two parallel plate in the mold filling process follows the equation:

$$\dot{\gamma} = \frac{6Q}{bh^2} \tag{4.1}$$

Where *b* is the width of the mold, *h* is the thickness of the mold, and *Q* was measured to be 1.92×10^5 mm³/s for the plaque mold at injection speed of 63.5 mm/s. The shear rate was calculated to be close to 2000 s⁻¹ for the plaque mold. ADXNB4 shows a much greater shear thinning behavior from low frequency to high frequency compared to ADXNC2 even though the *n* value at high frequency was close between ADXNC2 and ADXNB4.

4.3.2 The relationship of surface appearance to the morphology of the sample

The surface of the sample was smooth under optimized extrusion back pressure, pack pressure and melt temperature. The following section will first compare the cases with smooth surface and unsmooth surface and how they relate to the thickness and the cell structure. Then the cell morphology of the injection molded different composites foams with smooth surface at varied locations will be characterized.

4.3.2.1 The surface appearance, thickness variance and morphology

The thickness of the molded parts vs. location from the gate for the cases under optimized conditions for ADX and ADXNB4 and cases under unoptimized extrusion back pressures for ADXNC2 molded parts was characterized and has been plotted in Figure 4.6.



Figure 4.6 The thickness of the foam part vs. position from the gate for ADX, ADXNB4 under optimized conditions and ADXNC2 under extrusion pack pressure 2.8 MPa and 10.3 MPa (unoptimized conditions).

The thickness variation of the molded part from the gate to the end of the fill is within 0.04 mm for ADX and ADXNB4 with smooth surface. The thickness variation of the molded part for

ADXNC2 under 2.8 and 10.3 MPa extrusion back pressure was 0.18 mm. The extrusion back pressure facilitates the gas dissolution during the plastication process in the extruder and the filling stage to prevent bubbles early expansion. The surface appearance for ADXNC2 foam plaques under 2.8, 5.5 and 10.3 MPa extrusion back pressure have been presented in the Figure 4.7.



Figure 4.7 Surface appearance of injection molded foam plaques for ADXNC2 under extrusion back pressure at (a) 2.8 MPa (b) 5.5 MPa and (c) 10.3 MPa.



Two inadequately foamed regions on the molded part for ADXNC2 with 10.3 MPa extrusion back pressure were observed and non-uniform expansion of the molded part for ADXNC2 at 2.9 MPa extrusion back pressure was detected near the gate corners, making the middle case the best. The cell structure of the ADXNC2 injection molded under different extrusion back pressure was examined under SEM and have been presented in Figure 4.8.



Figure 4.8 Scanning electronic micrographs in TD-ND plane of ADXNC2 molded part under extrusion back pressure (a) 2.8 MPa; (b) 5.5 MPa; (c) 10.3 MPa at location C.



When the extrusion back pressure is too high, the remaining effect of the high extrusion back pressure can reduce the cell density and cell size as the material is injected in the mold. Low back pressure is not enough to prevent bubble pre-expansion in the extruder before the filling stage, also leading to collapsed cells. Even though the "patterns" on the surface of the molded part was less severe for 2.8 MPa extrusion back pressure case compared to 10.3 MPa case, the cell structure was not uniform. This indicates that surface smoothness may not necessarily guarantee uniform cell structure.

The effect of pack pressure on surface appearance, thickness variation and cell morphology was also investigated. Smooth surface was attained for ADXNB4 foamed part under two different pack pressures- 34.4 and 20.7 MPa, however, the thickness is more uniform for ADXNB4 molded part under 34.4 MPa pack pressure, with the thickness difference within 0.04 mm across the surface but the thickness varied from 2.8 mm to 2.6 mm for ADXNB4 part foamed under 20.7 MPa from location B to C. This is consistent with the trend that higher pack pressure leads to smaller shrinkage for the injection molded solid part. The injection molded foam plaques of ADXNB4 cross-section of normal to fill direction were characterized using SEM and have been presented in Figure 4.9 (Location C) and 4.10 (location B).



Figure 4.9 Scanning electronic micrographs in TD-ND plane of ADXNB4 molded part under pack pressure (a) 34.4 MPa and (b) 20.7 MPa at location C.

Figure 4.9 (Cont'd)



Figure 4.10 Scanning electronic micrographs in TD-ND plane of ADXNB4 molded part under pack pressure (a) 34.4 MPa and (b) 20.7 MPa at location B.

Figure 4.10 (Cont'd)



More collapsed bubbles were detected for molded part under 20.7 MPa pack pressure compared to that under 34.4 MPa pack pressure at both locations. More severe cell coalescence for the molded part under low pack pressure was detected even though the thickness and the surface appearance of the molded part was all smooth under two conditions at location B.

4.3.2.2 The cell structure of different composites with good surface appearance

The ADX and ADXNC2, and ADXNB4 were injection molded under the optimized molding conditions and the surface of the molded foam parts was smooth. The operating temperature for different composites was selected based on the shear rheology characterization in the previous section. The cell structure was examined under scanning electron microscope for three compounds at three different locations from the gate in the midway of the transverse direction – see Figure 4.11-4.13.



Figure 4.11 Scanning electron micrographs in TD-ND plane of ADX molded part at location (a) A (b) B and (c) C.



Figure 4.12 Scanning electron micrographs in TD-ND plane of ADXNC2 molded part at location (a) A (b) B and (c) C.



Figure 4.13 Scanning electron micrograph in TD-ND plane of ADXNB4 molded part at location A. The scanning electron micrograph for ADXNB4 molded part at location B and C are presented Figure 4.10 (a) and 4.9 (a), respectively.

The cell size and cell density for each composite at location A and B were similar for each composite and the cell structure at these locations were better than the cell structure at location C. This is attributed to a greater pressure drop between the melt and in the mold for initially filled melt compared to later filled melt, resulting in more severe cell coalescence in longer flow length. The nonuniformity in cell size and cell density at different locations was more severe for ADXNB4 molded part compared to ADX and ADXNC2 molded parts. The uniformity in cell size for ADXNC2 part at different locations was the greatest, even though the average cell size and cell density was not as good as ADXNB4 specimen. This could be due to that ADXNB4 sample has a lower extensional viscosity compared to ADXNC2, causing the melt strength not strong enough to prevent bubbles coalescence near the end of the fill location. The details of the cell size and cell density and the density of the part for each material at location B have been summarized in Table 4.5.

	Cell size, µm	Cell density, #/cc	Density, g/cc
ADX	101.4 ± 45.2	4.95×10^{5}	0.66
ADXNC2	103.2 <u>+</u> 42.6	4.51×10^{5}	0.67
ADXNB4	93.3 <u>+</u> 36.7	5.20×10^{5}	0.66

Table 4.5 Cell sizes and cell density under the optimized molding conditions at location B

The cell size distribution of the ADX, ADXNC2 and ADXNB4 under optimized conditions at location B were characterized and have been summarized in Figure 4.14. A narrower distribution was observed for ADXNB4 compared to ADX and ADXNC2.



Figure 4.14 Cell size distribution of (a) ADX and (b) ADXNC2 and (c) ADXNB4 molded part at location B under optimized foaming conditions.

Figure 4.14 (Cont'd)



The difference in cell size and cell density between ADXNC2 and ADXNB4 was mainly attributed to the melt temperature difference. The shear thinning property of ADXNB4 allowed a lower temperature profile for foaming compared to ADXNC2. This is consistent with previously reported that a low melt temperature contributed to a smooth surface of the molded part^[57] as well as smaller cell size and greater cell density^[20]. The cell density was similar for TPONC molded part compared to the ADX foam. This means that the effect of nanoclay on nucleation in talc-filled TPO is not very significant. This is probably due to the loss of the nucleation sites from the

aggregated talc particles, as well as talc particles migration from the PP and rubber interface to rubber phase after compounding, as well as the loss of the nucleation sites of the clay in the rubber phase.

4.3.3 Mechanical properties of molded tensile bar

4.3.3.1 Morphology

The molded tensile bars with the standard dimensions according to ISO 527 type 1 were molded for ADX and ADXNB4 under the same molding conditions listed in Table 4.3. It is worth noting here that the solid tensile bar for ADX and ADXNB4 was injection molded without core back stage with 4 mm thickness. The thickness of the ADX and ADXNB4 molded tensile bar foams was increased from 3 mm to 4 mm during core-back stage. The scanning electron micrographs in TD-ND planes of the molded tensile bars have been presented in Figure 4.15.



Figure 4.15 Scanning electron micrographs in TD-ND plane of the molded tensile bar under the same processing conditions (a) ADX magnification $37 \times$ (b) ADXNB4 magnification $37 \times$ at location 53 mm from the end closer to the gate.

Figure 4.15 (Cont'd)



A foam sandwich structure was detected with 3 mm thickness in foam region in the center and 1 mm for skin layers for both ADX and ADXNB4 foam (not shown on the SEM image). This is due to quick solidification of polymer melt near mold wall at lower temperature. The cell size, cell density and part density of the molded tensile bars for two composites have been summarized in Table 4.6.

Table 4.6 Properties of ADX and ADXNB4 molded tensile bar

	Cell size, µm	Cell density, #/cc	Density, g/cc
ADX	134.7 <u>+</u> 46.9	2.13×10^{5}	0.70
ADXNB4	117.6 <u>+</u> 42.9	3.41×10^{5}	0.71

The cell density was lower and the cell size was larger for molded tensile bar compared to the molded plaques for each composite, indicating that the larger mold opening distance may have an effect on the cell size. This may be attributed to a longer cell expansion time when the mold opening speed was fixed and the travel distance of the mold wall was increased. The average cell size was smaller and the cell density was greater for ADXNB4 foam compared to ADX foam. This may be attributed to that the strain hardening behavior in ADXNB4 prevented coalescence of bubbles in longer cell expansion process. The effect of the smaller pore size in ADXNB4 foam compared to ADX will be discussed further in the next section on mechanical properties.

4.3.3.2 Tensile test

The room temperature tested stress strain curves for various samples have been plotted in Figure 4.16.



Figure 4.16 Engineering stress vs. engineering strain tested at room temperature for ADX, ADXNB4 molded tensile bars and tensile bar foams.

Both tensile modulus and tensile strength decreased for tensile bar foams for both ADX and ADXNB4 due to the void fraction as expected, but both tensile strength and tensile modulus increased with addition of organoclay for both foamed and solid parts for ADXNB4 compared to the base ADX. The lower elongation at break property for ADXNB4 compared to ADX solid part was attributed to the degradation of the TPO during masterbatch and letdown process, the inclusion of low viscosity PP-g-MA as well as the aggregated talc particles after compounding with clay. Previous work reported that the masterbatch step was not used for TPO with organoclay additive to achieve better mechanical properties^[51], which confirms that the degradation of polymer attributed to lower elongation at break. The TPO with 3 wt% organoclay and 4.5 wt% PP-g-MA additive decreased the elongation from 400% by half even without the masterbatch step^[51]. Even though Chen *et al.*^[116, 117] reported that intercalated clay in the rubber phase with maleic anhydride modified EOC led to greater toughness due to increase energy due to delamination of clay particles, the aggregated talc particles were much larger compared to clay particles in the current study. Thus the lower elongation at break for ADXNB4 foam compared ADX foam was attributed to the lower elongation at break in the cell wall because a longer elongation to failure would be expected for smaller cells, as the crack propagation occurs at higher draw stress. The tensile modulus and tensile stress for the two foamed and unfoamed samples have been plotted in Figure 4.15 and 4.16, respectively.



Figure 4.17 Tensile modulus of ADX and ADXNB4 molded tensile bars and tensile bar foams.



Figure 4.18 Tensile strength of ADX, and ADXNB4 molded tensile bars and tensile bar foams. Because the tensile strength of the solid part for ADXNB4 was greater, the increased tensile strength of the foamed part could be due to the solid part instead of the cell structure, thus we had to compare the ratio of the foamed and unfoamed part for each composite. The details of the properties for ADXNB4 and ADX foamed part compared to solid part have been listed in Table 4.7.

	Tensile modulus of sandwich, GPa	Tensile strength σ , MPa	Elongation at break δ%	Sandwich E _f /E _s	Foam E' _f /E _s	σ_{f}/σ_{s}	$ ho_f ho_s$
ADX	1.22 ± 0.026	13.3 ± 0.14	16.5 ± 4.51				
ADX foam	0.78 ± 0.046	8.8 ± 0.33	30.8 ± 5.02	0.63	0.51	0.66	0.68
ADXNB4	1.22 ± 0.008	14.8 ± 0.05	97.4 ± 1.77				
ADXNB4 foam	0.86 ± 0.044	10.3 ± 0.25	11.5 ± 0.88	0.70	0.60	0.72	0.71

Table 4.7 The tensile properties of molded tensile bar specimens of ADX, ADXNB4 and their foams

The tensile modulus ratio of the foamed to unfoamed part for ADXNB4 compared to ADX is increased by 11% and the tensile strength ratio is increased by 9% with similar porosity level in

both foam parts. This means that the smaller cell size in ADXNB4 foam attribute to the increase in the tensile strength and tensile modulus of the foamed part compared to ADX foam. The ADXNB4 foam with smaller cell size could endure greater draw stress and thus the tensile strength is greater. The addition of organoclay improved the tensile modulus of the foam to be comparable to the microcellular TPO foams. The modulus of the foam sandwich structure is not the tensile modulus for the foam in the center region of the molded tensile bar. Based on the thickness of the skin (1.00 mm) and the tensile modulus of the solid part, the tensile modulus of the foam region was calculated to be 0.63 GPa for ADX and 0.73 GPa for ADXNB4, respectively. The ratio of the tensile modulus of foam and unfoamed polymer E'_{t}/E_s was revised to be 0.51 and 0.60 for ADX and ADXNB4 respectively. Thus an even greater increase (18%) was attained for the modulus ratio of foam and solid part for ADXNB4 compared to ADX. Even though previous study reported a higher tensile strength ratio (0.83) of the foamed and unfoamed TPO bars with less density ratio $(0.75)^{[21]}$, it would not be a fair comparison of the current results to the tensile properties of the microcellular TPO foams made by supercritical CO_2 because the mean cell size is typically less than 100 microns in the microcellular TPO foams.

4.3.3.3 Flexural test

The flexural test of the injection molded ADX and ADXNB4 unfoamed and foamed tensile bars have been plotted in Figure 4.19. The flexural modulus of the sandwich structure of ADXNB4 were improved by 10% compared to ADX sandwich structure.



Figure 4.19 The flexural modulus of ADX and ADXNB4 molded tensile bar foams.

4.4 Conclusions

For core-back foam injection molded 20 wt% TPO with vapor phase silane treated nanoclay additives, the PP-g-MA to clay ratio had to be increased to 2:1 (maleic anhydride grafted homopolymer PP) or 2.5:1 (maleic anhydride grafted copolymer PP) to ensure well dispersed nanoclay with strain hardening behavior. Meanwhile, it was challenging to maintain good dispersion of talc particles when dispersing the clay particles, as more aggregated talc particles were observed in TPO nanocomposites. The TPO nanocomposite with stronger shear thinning behavior allowed an operating temperature profile close to that used for the base TPO, leading to smooth surface and smaller cell size. The cell size increased with the mold opening distance on core-back displacement; this may be attributed to the longer time of cell expansion with a longer travel distance of the mold wall and the same mold opening speed. The tensile strength, tensile modulus and flexural modulus were tested to be greater for the foam injection molded TPO nanocomposites, which is attributed to smaller cell size.

Chapter 5. Morphology and Mechanical Strength of Die-Drawn Porous Sheets from Filled Polypropylenes

5.1 Introduction

Solid phase drawing of extruded sheets of neat or unfilled polypropylene (PP) or polyethylene (PE) materials has been developed to produce porous membranes^[68-71, 118-121]. The present work was motivated by the need to manufacture sheets of porous polypropylene with greater tensile strength than currently available. Thin porous polypropylene membranes are commonly used as battery separators. The stiffness and mechanical strength of the separator are tied to the thickness as well as the porosity. As the thickness is lowered, there is a need for greater tensile and puncture strength.

It is well-known that solid phase die-drawing of neat semicrystalline polymers leads to tenfold increases or higher in modulus and strength because of crystalline orientation^[82, 121-123]. Diedrawing of particulate filled polyolefins at elevated temperatures was developed recently to produce expanded and oriented particulate composites that are lighter and stronger after processing^[80, 106, 124, 125]. This process involves fitting an extruded feed billet into a heated converging die at temperatures that are 20°C to 30°C below the melting temperature and pulling at a high strain rate of the order of 0.1 to 1 s⁻¹. During die-drawing, the polymer debonds from the particles leading to growing voids near the tips or edges of the particles^[108, 126, 127]. This process leads to expanded composite materials with lower density and improved mechanical properties.

The draw ratio (DR) may be evaluated with eqn. 1.4 based on a steady state mass balance.

The linear draw ratio (LDR), or the strain of the billet measured in the MD (see eqn. 1.5), was used as the metric of the extent of drawing to be consistent with the terminology for solid-state drawing of thin film.

The linear draw ratio increases from the location near the die exit to the location near the belt puller where the maximum linear draw ratio is reached at a fixed draw speed. The maximum linear draw ratio that can be attained increases with draw speed, leveling off at higher draw speeds^[128]. With increasing linear draw ratio, the crystalline orientation and thus the modulus and tensile strength will increase also^[80]. The pulling force required increases with increasing strain and also with increasing strain rate^[83]. However, the material will break if the draw stress exceeds the strength of the material. The strength of the material is not only dependent on fibril formation from crystal orientation, but also the developed porosity and pore dimensions from debonded particles. Previous study reported that 60-70 % porosity developed in PP/glass fiber led to failure at low strain rate during die-drawing process^[80]. A porosity of 40-50 % could be attained for the drawn specimen^[80] with a thickness of at least 2 mm, but thinner sheets may break at a lower force, even before reaching the leveled off linear draw ratio with the maximum tensile properties. The mechanism of the breakage of the billet is crack propagation, and if the stress intensity factor, proportional to the applied draw stress and the square root of the initial crack length in TD is above a critical value, crack propagation will occur^[129]. Compared to tensile test at a strain rate of

 1×10^{-3} s⁻¹, the draw stress is greater during die-drawing process under a much greater strain rate (~1 s⁻¹), leading to a smaller critical crack length in TD during die-drawing process. The crack length in TD is the largest pore dimension in TD, and the pore dimension in TD is restricted by the particle dimension along TD. Thus the particle size is important to prevent the crack

propagation. However, few studies paid attention to the size of the particle, and the development of the pore dimension in TD during the die-drawing process.

The objective of this work was to examine die-drawn talc-filled polypropylene composite sheets of 1 mm thickness for morphology and mechanical properties using talc particles of different mean particle sizes. The die-drawing process was carried out at 128°C and 148°, and the characterization of properties were performed on the specimens taken from locations close to the belt puller with the maximum linear draw ratio at a certain draw speed.

5.2 Experimental details

The details of the composites prepared for this study have been presented in Table 5.1. Both polymers—PP5D37 (From Dow Chemical Co.) and PP 6025N (from Braskem) had a melting temperature of 168°C. The grades of talc in the two composites were Jetfil 290 (from Imerys Marble Inc.) with a median particle size of 8.5 μ m, labeled T8 here and BT2213 (from IMI FABI) with a median particle size of 10 μ m and labeled T10 here.

Table 5.1	Composition	before of	drawing

ID	PP Grade	Matrix MFI g-10 min ⁻¹	Talc vol%	Melting temp °C
H1T8	5D37	2.7	23	168
H2T10	6025N	2.5	24	168

It may be seen from comparing the cumulative particle size distributions presented in Figure 5.1 that T8 has a larger percentage of smaller particles. For example, the fraction of particles smaller than 3 microns is 20% in T8, and 13% in T10. It should be noted that the size in these figures is an equivalent spherical diameter.



Figure 5.1 Cumulative size distributions of the two grades of talc from manufacturers.

It may be seen from comparing the cumulative particle size distributions that have been presented in Figure 5.1 that T8 has a larger percentage of smaller particles. For example, the percentage of particles less than 3 microns is 20% in T8, and 13% in T10.

5.2.1 Die-drawing process

The materials were compounded with a twin screw extruder at 180°C and extruded to form billets with the help of Eovations, LLC, Bay City, MI. The billet thickness ranged from 4.0 to 4.6 mm and the die had an exit gap dimension of 2 mm. The width of the billets was unchanged in the
die at 40 mm but was reduced in the free draw region outside the die to 30 mm. The die drawing experiments were conducted in our laboratory at Michigan State University. The set-up schematic of the die drawing equipments has been presented in Figure 5.2.



Figure 5.2 Setup for die-drawing of a heated composite "billet" through a heated die; porosity, orientation and strength continue to develop along the free draw region outside the die.80 cm long sections of the billets were preheated in an oven (Grieve Model MT0559) and then

pulled through a heated die mounted on the outer wall of the oven by a Conair belt puller. The billet exiting the die was cooled by compressed air streams in the free draw region.

5.2.2 Mechanical characterization

Tensile test specimens (dog-bone shaped) were cut out from the billets before drawing directly with the help of a cutter. Several tensile specimens were cut from the drawn billets at different locations: 9.9, 25.1, 45.4, 75.9 and 106.4 cm from the die exit. Theses specimens were 14 cm long with a gauge length of 6.35 cm and were cut with the cutter placed in a Carver laboratory press and a force of 19.6 kN. Tensile tests were carried out on a UTS STM-20 test frame at room temperature at a strain rate of 5.08 mm/min following ASTM D638. A toe correction was applied to the engineering stress-strain curves and a secant modulus was calculated at 1% engineering strain. The undrawn polymer composites were tested according to ASTM D638 at room temperature at a strain rate of 5.08 mm/min after polishing the sample to be 14 cm long by

1.6 mm thick by 12.5 mm wide. The tensile test specimen of neat polymer matrix was prepared by a single screw extruder with a 0.5 mm thick by 25.4 mm wide slit die and the extrudates were cut into 152.4 mm long by 12.5 mm wide strips. The tensile tests were carried out on an Instron 5565 testing machine at 500 mm/min following ASTM D882.

Puncture penetration tests were performed against a sharp probe following ASTM F1306-90. The puncture test specimens were cut into 27 mm by 27 mm squares with the thickness measured by a micrometer. The specimen was placed in the center of the clamp with MD parallel to the longer dimension of the plate between two identical plates- see Figure 5.3.



Figure 5.3 Set-up for the puncture strength testing for die-drawn composites sheet between the two plates fixated by two bolts (not shown on the diagram).

5.2.3 Thermal characterization

The porosity of specimens was measured using a Sartorius YDK 01 density measurement kit, and the measurements were repeated three times. Samples of around 5 mg were cut from undrawn samples and sealed in aluminum pans for DSC testing on a TA analysis Q10 DSC. The samples were heated at 5°C/min to 128°C, then held there for a half hour before heating further again at 5°C/min. The crystallinity was calculate using the equation 2.2.

5.2.4 Morphological characterization

Scanning electronic microscopy (SEM) samples were scored in both the machine directionnormal direction (MD-ND) plane and MD-TD plane and immersed in liquid nitrogen for 30 min before fracturing, then coated with platinum or gold- see Figure 5.4.



Figure 5.4 Die-drawing specimen schematic for SEM samples in (a) MD-ND (b) MD-TD plane.

The SEM images were obtained using a JEOL 6610LV SEM. The pore size distribution of the drawn samples and the mean aspect ratio of the particles after compounding with polymer were analyzed using Image J software. The porosity of the die-drawn samples was characterized using a Sartorius YDK 01 density kit.

5.3 Results

5.3.1 Characterization of the undrawn samples

The engineering stress-strain curves in tension at room temperature have been plotted for the undrawn composites H1T8, H2T10 and the neat polymer H1 and H2 in Figure 5.5. The tensile specimens were tested till failure.



Figure 5.5 Room temperature tested stress-strain curves of undrawn composites samples (at 1×10^{-3} s⁻¹) and polymer matrix samples (at 0.1 s⁻¹).

The elongation at break was lower for composites compared to the neat polypropylene for both H1T8 and H2T10, which is consistent with previous studies on lower elongation at break for composites filled with micron sized talc or spherical particles^[109, 130]. The elongation at break is similar for the two polymer matrices and the composites. This is related to weak adhesion between the talc particles and polymer matrix. When the stress is applied on the polymer matrix, no adequate stress transfer occurs from the polymer to the rigid particles. When the potential energy near the particle surface is greater than the work of adhesion between the particles and the polymer matrix, voids will be created near the tips or edges with the most concentrated stress. The debonding stress is predicted by the energy balance between the potential energy near the particle surface and the work of adhesion between the two phases by Vollenberg *et al.* ^[110] illustrated in eqn. 1.7. For the spherical particles, the debonding stress is proportional to $1/R^{1/2}$ and the greater particles tend to be debonded from polymer under a lower stress, and the polymer debonds from the particle only within elastic region^[108].

The details of the yield stress for unfilled H1 and H2 polymer and the composites were summarized in Table 5.2 and the yield stress decreased for composites compared to neat PPs.

Material	H1T8	H2T10
σ_{ym} , MPa	36.1	39.9
σ_{yc} , MPa	32.1	28.0
Average aspect ratio of particles	5.7	5.9

 Table 5.2 Composites properties before drawing

This is consistent with what Zhou *et al.*^[131] reported for talc filled PP and Shipley *et al.* reported for glass flake and glass beads filled PP^[132]. A decrease in yield stress for composites was observed with micron size fillers while a greater yield stress was reported for nanocomposites^[131, 133]. In micron size range, the reduction in adhesion leads to a lower yield stress because of the stress amplifying effect in the polymer region near the particles^[103, 134]. Thus a lower macroscopic stress applied to the composite could cause yielding of the polymer. However, for nanofillers, a greater yield stress is attributed to the strong adhesion between nanoparticles and polymer matrix without debonding process. Also, the yield stress of the composites were reported to decrease as the filler size increased in micron range^[133], and this is consistent with the greater yield stress for H1T8 compared to H2T10 even though the yield stress of H2 is greater than H1. The undrawn composites in fractured MD-ND plane were detected by SEM and have been presented in Figure 5.6.



Figure 5.6 Backscattered electron micrographs in fractured MD-ND plane of the undrawn (a) H1T8 and (b) H2T10 after annealing for 0.5 hr at 128°C.

A greater number of large particles were observed for H2T10 compared to H1T8 undrawn specimen in fractured MD-ND plane. The aspect ratios (length over thickness) of the T8 and T10 particles measured from Figure 5.6 have been presented in Table 5.2. The aspect ratio of the particle is similar for T8 and T10, excluding the different effect on the tensile strength from the undebonded particles for the two specimens.

5.3.2 Limiting linear draw ratios and draw speeds

The maximum linear draw ratio or strain obtained will vary with draw speed and temperature for each composite^[80]. The nominal draw ratio is the cross-section area ratio of the

billet and the die exit. The maximum linear draw ratios have been plotted against draw speed for two composites drawn at 128°C and 148°C in Figure 5.7.



Figure 5.7 Maximum linear draw ratio vs. draw speed for H1T8 and H2T10 drawn at (a) 128°C and (b) 148°C.

The maximum linear draw ratio for each composite drawn at 148°C increased and leveled off as draw speed increased -see Figure 7 (b). This is consistent with previous report for talc filled PP^[128] and neat PP^[78, 135]. The upper end of the draw speed range appearing on each curve drawn at 128°C in Figure 7 (a) signifies the limiting speed at which the billets could be drawn without breaking. The linear draw ratio increases with the draw speed for both composites but the maximum linear draw ratio was much higher for H1T8 composite compared to H2T10 at 128°C. The fracture of the billet near the die exit led to breakage of the billet. At 148°C, the load was stabilized at higher strain rates due to the ability of the polymer to leave the die wall at optimized location and a lower contact area between the billet and the die^[78] while at 128°C, the contact area between the billet and the die use stabilized to the drawn billet is dependent on the development void fraction, the crystallinity rearrangement and initial crack length in the billet. The void fractions.

The void fraction for the final product vs. the maximum linear draw ratio for the two composites have been plotted in Figure 5.8.



Figure 5.8 The void fraction vs. maximum linear draw ratio of the die-drawn H1T8 and H2T10 composites at (a) 128°C and (b) 148°C.

The porosity is consistently higher for H2T10 compared to H1T8 at both 128°C and 148°C; this is attributed to the greater portion of particles debonded under a lower draw stress in H2T10. The porosity level is the same for the two composites at 128°C and respective limiting linear draw ratios. The slower developed porosity could also attribute to a greater limiting maximum linear draw ratio for H1T8 composite, as the lower porosity developed at lower strains prevented early breakage of the polymer. The void fraction increased and leveled off for both H1T8 and H2T10

composites at 148°C. The lower leveled off porosity for H1T8 compared to H2T10 is attributed to the stabilized draw stress without debonded smaller particles.

The void fraction was lower for each composite after die-drawing at higher temperature; this may be attributed to the decreased yield stress of both amorphous and semi-crystalline polymer matrix at a higher temperature by Erying's model^[102]. At higher temperature, polymer tends to yield at a lower macroscopic load and the smaller particles could not be debonded without enough energy to overcome the work of adhesion to the polymer, leading to less void fraction. This explains a lower final porosity at 148°C compared to 128°C for each of the composite. This is consistent with previously reported that the porosity of the drawn material at lower temperature for PP composites was greater^[80]. The crystallinity and crystal orientation of the undrawn and drawn specimen was assessed in the following section.

5.3.3 Crystallinity and crystal orientation

The degree of crystallinity before drawing and after die-drawing at limiting linear draw ratios were evaluated with the DSC using a heating rate of 5°C/min after annealing at 128°C for 0.5 hr. The crystallinity of PP in the composite was 55% for H1T8 and 53% for H2T10 at limiting speeds (see Table 5.3).

Material	H1T8	H2T10
Crystallinity before drawing %	48	49
Crystallinity after drawing %	55	53

Table 3 Crystallinity before and after drawing

The crystallinity before drawing and after drawing was similar for the two composites. The increase in crystallinity after die-drawing process has been reported by Chaffey *et al.*^[122]. This is

attributed to disentangled amorphous chains recrystallization process under high temperature below the melting temperature^[104, 105] at high strains. The cross-hatched spherulites with tangential and radial lamellae in PP crystalline are broken into lamellae by intra-lamellar shearing or smaller fragments by inter-lamellar shearing during drawing process^[106, 136]. The crystals from spherulites breakup are transformed into fibrils with great mechanical properties at higher strains. The presence of talc in PP composites reduced the spherulites size and introduces transcrystalline (columnar crystal) near the particle surface^[85, 88, 137, 138]. The similar crystallinity indicates the same level of crystalline region contributed by both spherulites and transcrystalline for the two composites. Compared to spherulites, the transcrystalline is broken into lamellae and transforms to fibrils at higher draw ratios^[106]. In the current study, the most stable form of crystal in isostactic PP is α -form, which has a monoclinic unit cell with adjusted orthogonal axes labeled a^* , b and c. Previous work has shown that the *b*-axes of PP crystals tend to be oriented along the ND with talc additives. A quantitative comparison for the degree of c-axis orientation is characterized by Herman orientation parameter. The average angle between c-axis with MD obeys eqn. 5.5^[139]:

$$\langle \cos^2 \phi_{cM} \rangle = \frac{\int_0^{2\pi} \int_0^{\frac{\pi}{2}} I(\varphi, \chi) \cos^2 \varphi \sin \chi^3 d\chi d\varphi}{\int_0^{2\pi} \int_0^{\frac{\pi}{2}} I(\varphi, \chi) \sin \chi d\chi d\varphi}$$
(5.5)

Herman orientation parameters for c-axis orientation in MD were computed using eqn. 5.5 and $5.6^{[139]}$.

$$f_{cM} = \frac{3\langle \cos^2 \phi_{cM} \rangle - 1}{2} \tag{5.6}$$

The f_{cM} was computed to be 0.6 on average for H1T8 drawn at 9.0 final linear draw ratio and 0.7 on average for H2T10 drawn at 7.6 final linear draw ratio. This indicates that the degree of c-axis orientation along MD is similar in the two cases. However, the extent of crystalline rearrangement to form fibril may still be greater at higher linear draw ratio for H1T8 because the c-axes of both transcrystals and the crystals in fibril are oriented along the machine direction.

5.3.4 Morphology of the die-drawn specimens

The pores created around debonded particles during die-drawing may be seen in the scanning electron micrographs in MD-TD fractured plane for the two composites drawn at similar linear draw ratios in Figure 5.9.



Figure 5.9 Scanning electron micrographs in fractured MD-TD plane of die-drawn (a) H1T8 at linear draw ratio=5.7 (b) H2T10 at linear draw ratio=6.4 and 128°C. The largest dimension of stacked voids along TD was marked by the blue arrow.

The pores in MD and TD are greater for H2T10 compared to H1T8 drawn specimen. Stacked voids along TD were observed in both composites, thus the largest dimension along TD of stacked voids instead of the individual void determined the crack length when no actual crack existed initially, and H2T10 had a greater initial crack length in TD. Since the pore dimension in TD is restricted by the particle dimensions in width direction, the initial crack length during the die-drawing process is also equal to the largest TD dimension of stacked particle, which is greater for T10 particles. The crack propagation will occur if the sum of negative elastic strain energy and the work of formation of crack decreases with the increase in crack length. A stress intensity factor *K* proportional to the draw stress and the square root of crack length has been introduced and the crack propagation occurs when *K* is greater than a critical value $K_c^{[129]}$. Thus with a smaller initial crack length in TD for H1T8, the critical draw stress leading to crack propagation could be greater at higher draw speed. Thus the greater limiting maximum linear draw ratio for H1T8 may be attributed to the smaller initial crack length in TD as well as a slower developed porosity. The dimension of pore in MD has been plotted against maximum linear draw ratios in Figure 5.10.



Figure 5.10 Mean MD dimension of pore vs. maximum linear draw ratio for H1T8 and H2T10 die-drawn samples at 128°C.

The mean MD dimension of pore was higher at a greater maximum linear draw ratio for each drawn composite, which was caused by the greater void growth process under larger draw stress. The average pore dimension in MD was greater for H2T10 sample compared to H1T8 at similar linear draw ratios; this could be attributed to that the polymer yielding point was achieved at lower draw stress with greater filler sizes and the void growth happened at lower strain for larger particles, as well as the greater initial pore dimension in MD (same as particle size in MD) for larger particles. The details of the mean pore dimensions in other directions and the aspect ratio of the pore (MD/TD) have been summarized in Table 5.4.

Materials	Draw speed m/min	Maximum linear draw ratio	Mean TD dimension of pore µm	Mean ND dimension of pore µm	Mean aspect ratio of pore
	1.6	5.7	7.8	1.8	8.5
H1T8	3.8	8.3	8.3	2.5	9.3
	5.5	9.2	9.0	2	10.4
	1.8	6.3	12.3	3.2	8.1
H2T10	2.3	6.8	12.5	3.3	9.2
	2.9	7.6	11.9	4	10.5

Table 5.4 Measured properties of two composites after drawing

The mean aspect ratio of pore and the mean ND dimension of pore were similar for both die-drawn composites. Thus the pore aspect ratio was not the reason for H1T8 that could be drawn to a higher limiting maximum linear draw ratio. Both mean pore dimension in ND and TD were not changing with the maximum linear draw ratio; this was attributed to that the pores created were restricted by the particle dimensions in ND and TD. The mean TD dimension of pore was greater for H2T10 sample as expected.

5.3.5 Mechanical properties

The engineering stress-strain curves in tension at room temperature have been plotted for the drawn composites H1T8 and H2T10- drawn at different draw ratios or draw speeds- see Figure 5.11. The die-drawn tensile specimens were tested till failure.



Figure 5.11 Room temperature tested (at $1 \times 10^{-3} \text{ s}^{-1}$) stress-strain curves of H1T8 and H2T10 after die-drawn at 128°C.

The engineering stress strain curves were very similar for two composites at similar draw ratios and the elongation at break for the drawn specimens was much greater compared to the undrawn specimens; this is consistent with previously reported that orientation in polymer could reduce the brittle fracture of the composite with the specimen after rolling process ^[134]. The tensile strength and secant modulus at 1% vs. at different linear draw ratios at both 128 and 148°C have been plotted in Figure 5.12 and 5.13, respectively.



Figure 5.12 Tensile strength results from static tensile test (at $1 \times 10^{-3} \text{ s}^{-1}$) on die drawn samples of H1T8 and H2T10 drawn at (a) 128°C and (b) 148°C.



Figure 5.13 Secant modulus results from static tensile test (at 1×10^{-3} s⁻¹) on die drawn samples of H1T8 and H2T10 drawn at (a) 128°C and (b) 148°C.

The tensile strength increased with the linear draw ratio and leveled off for each composite at 148°C, which is consistent with previous report on neat polymers^[77, 82, 128]. Both tensile strength and modulus increased with the maximum linear draw ratio drawn at 128°C for two composites without leveling off. A similar trend was reported on the die-drawn wood flour filled PP by Cai *et al.*^[140]. At the limiting maximum linear draw ratio, a greater tensile strength and tensile modulus were observed for H1T8 compared to H2T10 at the same porosity level. The draw stress was much lower for tensile test under a low strain rate (1×10⁻³ s⁻¹) compared to die-drawing process under a

high strain rate (1 s⁻¹), and with the critical stress intensity factor K_c to be 2.47 MPa-m^{1/2} for PP and 20 vol% talc composites^[141], the critical crack length to promote crack propagation was much greater than the stacked voids in TD. Thus the higher tensile strength could only be attributed to a greater extent of crystalline rearrangement to fibrils for drawn H1T8 composite at greater limiting linear draw ratio, despite the fact that Herman orientation parameter was similar for H1T8 and H2T10 at the respective limiting linear draw ratio. The anisotropic ratio of the pore could also lead to a greater tensile strength of brittle polymer materials^[142], but the anisotropic ratio or aspect ratio of the pore was similar for the two drawn specimens (see Table 5.3).

The tensile modulus increased continuously as the maximum linear draw ratio increased at both temperatures. A higher tensile modulus was observed at lower temperature for each composite, which is consistent with previous study on both PP^[82] and talc filled PP composites^[128]. Room temperature tested force vs. penetration depth curves in puncture tests have been plotted for two composites after drawn at similar linear draw ratios-see Figure 5.14.



Figure 5.14 Force vs. penetration curves of die-drawn H1T8 and H2T10 specimens 115 cm from die exit after die-drawing at different final linear draw ratios.

A higher maximum force was observed for H1T8 compared to H2T10 specimen after drawn at similar linear draw ratios. The thickness of the two drawn specimens at different maximum linear draw ratio has been presented in Figure 5.15.



Figure 5.15 The thickness of the die-drawn H1T8 and H2T10 composites at (a) 128°C and (b) 148°C and the maximum linear draw ratio.

The thickness decreased with the maximum linear draw ratio as expected. The thickness of the H1T8 specimen was greater compared to H2T10 sample except at the limiting maximum linear draw ratio. At the limiting maximum draw ratio, the thickness of the die-drawn specimen was similar for the two drawn specimens with the same density reduction level, and this was attributed to a greater reduction in width for H1T8 specimen with greater maximum linear draw ratio.

The puncture strength, defined by the ratio of the maximum force over thickness, was computed for the die-drawn samples at different maximum linear draw ratios to exclude thickness factor. The punctures strength vs. maximum linear draw ratio corresponding to varied draw speeds for both composites have been plotted in Figure 5.16.



Figure 5.16 Room temperature tested puncture strength vs. maximum linear draw ratio for H1T8 and H2T10 drawn at 128°C.

The puncture strength decreased with maximum linear draw ratio but leveled off at higher linear draw ratio for H1T8 sample while the puncture strength kept decreasing as the draw ratio increased for H2T10 sample. Previous study has reported that the puncture strength decreases as the linear draw ratio increasing for HDPE film stretching^[143]. The puncture strength is related to pore size^[144], the pore size distribution^[143, 144] and mechanical strength of the film^[143, 144] with a fixed probe diameter and probe angle as well as unchanged friction between the probe and the specimen^[144]. The puncture strength was consistently greater for H1T8 compared to H2T10 at all linear draw ratios. This may be attributed to the greater pore dimensions in MD and TD for H2T10. At the respective limiting maximum linear draw ratios for the two composites with the same porosity level, a higher puncture strength for H1T8 compared to H2T10 is attributed to a smaller mean pore dimensions in both MD and TD as well as the greater extent of crystalline transformation to fibrils in polymer matrix. The greater fibrils formation also compensated the effect of increased mean pore dimension in MD for a leveled off puncture strength in H1T8 at the higher maximum linear draw ratio.

5.4 Conclusions

The pore volume fraction and the mechanical properties of two talc-filled polypropylenes with different particle size distributions of talc have been compared after die-drawing at 128°C and 148°C at different draw ratios. The limiting maximum linear draw ratio levels off as draw speed increasing at 148°C as previously reported but at 128°C, the limiting maximum linear draw ratio without breaking was higher for the composite with the smaller mean particle size; this may be attributed to the slower developed porosity as well as smaller TD dimension of stacked voids obtained with this material. At the respective limiting linear draw ratios, the porosity level is the same for both composites but the composite with the smaller talc particle sizes and higher draw ratios led to drawn sheets with greater tensile strength and greater puncture strength. The greater tensile strength may be attributed to greater crystalline rearrangement to fibrils in the composite while the higher puncture strength is caused by smaller pore dimensions in both MD and TD as well as greater crystalline rearrangement to fibrils.

Chapter 6. Conclusions and Recommendations

The present study was separated into two parts and the conclusions and recommendations for each part as follows:

6.1 Part I

6.1.1 Conclusions

The first part of the research was motivated by the need to produce recyclable lighter and thinner injection molded thermoplastic polyolefin (TPO) foam parts for automotive interiors by chemical foaming agent. This was achieved by modifying the talc filled TPO compound with organoclay additive that not only controlled the cell size to be smaller and more uniform, but also attained a smooth surface of the foamed parts. The objectives of this research were (1) to investigate the effect of different level of vapor phase silane coupling agent treatment on increasing the *d*-spacing of organoclay and the extent of dispersion in polypropylene; (2) to understand the relationship between melt rheology, surface appearance, foam morphology and mechanical properties of foam injection molded talc filled TPO and organoclay additive with optimized level of vapor phase silane pretreatment.

TPO nanocomposites were prepared with organically modified montmorillonite, a silane coupling agent, maleic anhydride grafted polypropylene as compatibilizer and a commercial grade TPO with 23 wt% talc loading. The organoclay was treated with 0.8 wt% of the vapor phase silane coupling agent to improve the interaction between the clay and the TPO to reduce the usage of low viscosity compatiblizer. For core-back foam injection molded 20 wt% TPO with vapor phase silane treated nanoclay additives, the PP-g-MA to clay ratio were increased to 2:1 (maleic anhydride grafted homopolymer PP) or 2.5:1 (maleic anhydride grafted copolymer PP) to ensure well dispersed clay and strain hardening behavior. Compared to PP/clay nanocomposites with a

PP-g-MA to clay ratio of 1:1, the increased PP-g-MA amount in TPO nanocomposites served as the compatibilizer for talc particles also. Meanwhile, it was challenging to maintain good dispersion of talc particles when dispersing the clay particles, as more aggregated talc particles were observed in TPO nanocomposites. The TPO nanocomposite with stronger shear thinning behavior allowed an operating temperature profile close to that used for the base TPO, leading to smooth surface and smaller cell size. The cell size increased with the mold opening distance on core-back displacement; this may be attributed to the longer time of cell expansion with a longer travel distance of the mold wall and the same mold opening speed. The tensile strength, tensile modulus and flexural modulus were tested to be greater for the foam injection molded TPO nanocomposites, which is attributed to smaller cell size.

6.1.2 Recommendations

The commercial TPO grade used for this study is filled with 23 wt% talc loading. The 23 wt% filled TPO was used as the flow control component in masterbatch step of compounding to provide enough shear force for delamination of clay. After letdown step, more aggregated talc clusters were discovered, and the elongation at break was lowered for the injection molded TPO nanocomposites without foaming. The low viscosity PP-g-MA, and the degradation of the polymer matrix could also reduce the elongation at break. Thus the future work could be focusing on: i) improving the dispersion of both talc and clay with less PP-g-MA compatibilizer; ii) targeting the locations for clay and talc during compounding to be mostly in PP phase; iii) applying an unfilled TPO grade with proper melt flow index without talc filler to achieve a better dispersion of clay in the masterbatch step with lower usage of PP-g-MA compatibilizer; iv) adding organoclay additive during TPO production instead of reprocessing TPO four times in the TPO nanocomposites system- extrusion compounding of TPO with talc, masterbatch, letdown, and extrusion for FIM;

v) selecting different fillers other than clay to keep high impact properties. For example, adding two types of talc with different sizes to have the larger particles to prevent shrinkage during FIM and smaller particles to be nucleation sites.

6.2 Part II

6.2.1 Conclusions

The pore volume fraction and the mechanical properties of two talc-filled polypropylenes with different particle size distributions of talc have been compared after die-drawing at 128°C and 148°C at different draw ratios. The mechanical properties of specimens drawn at 148°C was consistent with previous work but at 128°C, the limiting maximum linear draw ratio without breaking was higher for the composite with the smaller mean particle size; this may be attributed to the slower developed porosity as well as smaller TD dimension of stacked voids obtained in this material. At the respective limiting linear draw ratios, the porosity level is the same for both composites but the composite with the smaller talc particle sizes led to drawn sheets with greater tensile strength and greater puncture strength. The greater tensile strength may be attributed to greater crystalline rearrangement to fibrils in the composite while the higher puncture strength is caused by smaller pore dimensions in both MD and TD as well as greater crystalline rearrangement to fibrils.

6.2.2 Recommendations

Currently, the thickness of the die-drawn sample is 1 mm and not low enough as a battery separator membrane without post treatment. The thickness of the battery separator is 400 μ m for NiMH batteries and 25 μ m for Li-ion batteries. A lower thickness in the drawn product requires reducing the die exit gap. The current undrawn billet is 4 mm thick and the die exit gap is 2 mm with a nominal draw ratio of 2 (width of the billet not restricted by the die). If using the undrawn

billet with the current thickness, a lower die exit gap or greater nominal draw ratio for the die is needed. However, the limiting linear draw ratio for a greater nominal draw ratio is lower with higher stress on the billet near the die exit. Meanwhile, when the thickness of the drawn billet is reduced but the porosity is the same, the billet could break at low linear draw ratios. Thus there is a limitation on the porosity, thickness and the tensile strength of the material and filler size. Future work could focus on i) measuring the draw stress by modifying the drawing line with a force measurement device; ii) modeling the draw stress and tensile strength of polymer changing with linear draw ratio at different nominal draw ratios and die exit gaps during drawing process to predict the limits on the final thickness, porosity and filler size; iii) modeling the puncture strength and tensile strength with crystalline rearrangement to fibrils, porosity and pore size distribution. BIBLIOGRAPHY

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