

TRANSPARENT, BIAXIALLY ORIENTED BARRIER FILMS FROM
POLYPROPYLENE-CLAY NANOCOMPOSITES

By

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ABSTRACT

TRANSPARENT, BIAXIALLY ORIENTED BARRIER FILMS FROM POLYPROPYLENE-CLAY NANOCOMPOSITES

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The research work is divided into three sections – (i) transparent barrier films, (ii) high expansion foams and (iii) transparent molded panels, all from polypropylene clay nanocomposites. Biaxially oriented polypropylene (BOPP) is used for transparent, flexible high-barrier packaging film. The biaxial orientation process improves the barrier to gases and the mechanical properties by rearrangement of the crystal structure. Polymer nanocomposites incorporating layered nanofiller have the potential to provide striking enhancements in barrier to water vapor and oxygen. However, there is a conflict between addition of nanoclay and stretchability in the BOPP process where rapid deformation and high stress are experienced. In this work, we demonstrated successful achievement of both stretchability and property improvements after incorporating an innovative masterbatch additive based on nanoclay into polypropylene. The maximum area stretch ratio of 7×7 achieved without film breakage during biaxial stretching of nanocomposite was as high as that obtained with the unfilled or neat polypropylene. Transmission electron micrographs and dynamic shear rheology revealed that the extent of dispersion of nanoclay in polypropylene was improved after the biaxial stretching. Small angle X-Ray scattering revealed that the crystalline lamellar thickness in the BOPP-NC was larger than in BOPP. Furthermore, the crystalline orientation was more evenly distributed in the plane of the BOPP-NC film as seen from 2D-SAXS images while the degree of crystallinity was seen to be very similar in BOPP and BOPP-NC from wide angle X-Ray diffraction (WAXD). As a result, BOPP nanocomposite film with significantly enhanced

stiffness and barrier to both water vapor and oxygen was achieved without sacrificing transparency. In addition, the simultaneous and sequential biaxial stretching behavior of these nanocomposite under processing conditions relevant to industry practice were compared. It was found the characteristic deformation behavior differs significantly between two stretching modes. 2D SAXS revealed the morphology difference in terms of lamellar orientation where a more isotropic in-plane orientation was found in simultaneously stretched films and a preferential alignment along the two stretching directions especially TD was found in sequentially stretched films.

In the second section, polypropylene nanocomposites were evaluated with batch foaming using supercritical CO₂ in a pressure vessel. An ultra-high expansion ratio of 35.8 was achieved which can be ascribed to two factors: 1) The high melt strength and strain hardening behavior by addition of nanoclay helps the nanocomposite foam cell withstand the high expansion force allowing for a relatively larger cell size capability. 2) The nanoclay also increased the cell density significantly. It is found that biaxial expansion induced orientation and improved delamination of nanoclay. Consequently, the nanocomposite foam exhibited a well-defined cell structure compared to foamed PP.

Finally, incorporation of the same nanolayers with selected proportions of compatibilizer in thermoplastic olefin blends or blends of polypropylene homopolymer with toughening copolymers of ethylene and propylene yielded significant improvements in the transmission of light and reduction of haze through molded panels of the multiphase composite compared to molded panels from the unfilled blends.

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DEDICATED
TO
MY PARENTS ZHONGSHU LU & CUIZHEN HU

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TABLE OF CONTENTS

LIST OF TABLES	xi
LIST OF FIGURES.....	xii
Chapter 1. Background.....	1
1.1 Biaxially oriented polypropylene clay nanocomposites barrier film.....	2
1.1.1 Research background and motivation	2
1.1.2 Biaxial orientation: a general introduction.....	3
1.1.3 Biaxially oriented polypropylene (BOPP): processing and structure development ..	10
1.1.4 Barrier in biaxially oriented polypropylene (BOPP)	16
1.1.5 Polymer nanocomposite	18
1.1.6 Polymer nanocomposite for improved barrier	24
1.1.7 Biaxially oriented nanocomposite film	26
1.1.8 Research Objective and Hypotheses	29
Chapter 2. Materials and Experimental Procedures	31
2.1 Materials	31
2.2 Nanocomposites Preparation and Processing	32
2.2.1 Nanocomposite Preparation	32
2.2.2 Biaxial stretching	32
2.2.3 Supercritical Batch Foaming.....	33
2.2.4 Injection molding and compression molding.....	34
2.3 Characterization techniques.....	35
2.3.1 Rheology	35
2.3.2 Thermal Analysis	37
2.3.3 Transmission Electron Microscopy	38
2.3.4 Scanning Electron Microscopy	39
2.3.5 X-ray Diffraction (XRD)	41
2.3.6 Small Angle X-ray scattering.....	42
2.3.7 Permeability Measurement	43
2.3.8 Optical Property Measurement	44
2.3.9 Mechanical Property Measurement	45
Chapter 3. High-Barrier Film from Biaxially Oriented Polypropylene Clay Nanocomposites: Structure and Properties	46
3.1 Introduction	46
3.2 Materials and Characterization	49
3.2.1 Materials.....	49
3.2.2 Nanocomposite Processing	50
3.2.3 Biaxial Orientation	50
3.2.4 Characterization	51
3.3 Results and Discussion	53
3.3.1 Biaxial stretching behavior	53

3.3.2 Stretched film appearance	55
3.3.3 Nanoclay dispersion	57
3.3.4 Crystal structure	61
3.3.5 Mechanical property	70
3.3.6 Barrier property.....	72
3.4 Conclusion	76
Chapter 4. Comparison of Simultaneous and Sequential Biaxially Oriented Polypropylene Nanocomposite Films	78
4.1 Introduction	78
4.2 Materials and Characterization	83
4.2.1 Materials.....	83
4.2.2 Nanocomposite preparation	84
4.2.3 Biaxial Stretching.....	85
4.2.4 Characterization	86
4.3 Results and Discussion	87
4.3.1 Biaxial stress-strain behavior	87
4.3.2 Stretched film appearance.....	95
4.3.3 SAXS	98
4.3.4 Mechanical property	101
4.3.5 Barrier property.....	104
4.4 Conclusions	105
Chapter 5. Ultra-high expansion PP Nanocomposite Foam under supercritical CO₂: Rheology, Deformation, Structure, and Mechanical	107
5.1 Introduction	107
5.2 Materials and Characterization	111
5.2.1 Materials.....	111
5.2.2 Nanocomposite preparation	111
5.2.3 Batch foaming.....	112
5.2.4 Characterization	113
5.3 Results and discussion	115
5.3.1 Foam expansion	115
5.3.2 Cellular structure.....	117
5.3.3 Clay dispersion.....	119
5.3.4 Extensional rheology.....	121
5.3.5 Biaxial deformation behavior.....	123
5.3.6 Compressive behavior of foams.....	126
5.4 Conclusions	129
Chapter 6. Additives and Blends for Translucent Thermoplastic Polyolefin (TPO) Automotive Bumper Fascia	130
6.1 Introduction	130
6.2 Materials and Characterization	133
6.2.1 Materials.....	133
6.2.2 Blends and nanocomposite preparation	134

6.2.3 Characterization	134
6.3 Results and Discussion	135
6.3.1 Effect of nano CaCO ₃ on TPO1	135
6.3.2 Contact Angle	136
6.3.3 Effect of SEBS on TPO1	138
6.3.4 TPO with selected PP, rubber and additives	138
6.3.5 Effect of thickness.....	139
6.4 Conclusions	141
Chapter 7. Conclusions and Recommendations	142
7.1 Biaxially oriented nanocomposite film.....	142
7.1.1 Conclusions.....	142
7.1.2 Recommendations.....	143
7.2 A look into sequential biaxially stretched nanocomposite film from a continuous line	145
7.2.1 Observation and discussion.....	145
7.2.2 Recommendations.....	149
7.3 Nanocomposite Foam	150
7.3.1 Conclusions.....	150
7.3.2 Recommendations.....	150
7.4 TPO nanocomposite	152
7.4.1 Conclusions.....	152
7.4.2 Recommendations.....	152
BIBLIOGRAPHY	155

LIST OF TABLES

Table 3.1 Compositions of PP/clay nanocomposites.	50
Table 3.2 Effective aspect ratio of clay nanolayers	61
Table 3.3 Estimated Crystallinity and crystallite size (D_{040}) of PP and nanocomposite before and after stretching	63
Table 3.4 Oxygen permeability of extruded sheets before stretching and biaxially oriented films after stretching	73
Table 3.5 Water vapor permeability of biaxially oriented films after stretching	73
Table 4.1 Compositions of PP/clay nanocomposites	85
Table 5.1 Expansion ratio, average cell size and cell density of PP and nanocomposite foam .	116
Table 5.2 Maximum strain hardening ratio for polymer melt at 180	123
Table 6.1 Effect of CaCO_3 and SEBS on optical performance of TPO1	135
Table 6.2 Optical and mechanical properties of selected TPO	139

LIST OF FIGURES

Figure 1.1 Schematic of tenter-frame biaxial orientation process (top view, insert is cross-section view).	5
Figure 1.2 Schematic of double bubble process.	7
Figure 1.3 Schematic of biaxial rigs and two stretching modes.	9
Figure 1.4 Tortuous diffusion pathway created by parallel arranged uniform rectangular platelets.	24
Figure 3.1 Representative stress-strain curve of PP and PPNC during simultaneous biaxial stretching at 156 °C (equally along MD and TD at 200% s ⁻¹).	55
Figure 3.2 Optical performance of 25-micron thick BOPP and BOPPNC films, (a)top: optical appearance of representative BOPPNC5 film; (b) bottom: transmittance of 25-micron thick BOPP and BOPPNC films.	56
Figure 3.3 Thickness profile along MD and TD in various films.....	57
Figure 3.4 TEM of PPNC5 (a) before stretching and (b) BOPPNC5 after stretching, scale bar 0.2µm.	58
Figure 3.5 Dynamic Shear Rheology of PPNC before stretching and BOPPNC after stretching (a) storage modulus (b) dynamic viscosity.....	59
Figure 3.6 WAXD patterns of PP and nanocomposites (a)Extruded (b)Biaxial stretched.	62
Figure 3.7 2D SAXS pattern of PP and nanocomposites before and after stretching.....	64
Figure 3.8 1D SAXS intensity profile of PP, nanocomposites and clay (a) Extruded (b) Biaxial stretched (c) Clay.	66
Figure 3.9 Schematic illustration of dimension parameters to describe a lamellae crystal.	67
Figure 3.10 Lamellar thickness and lateral dimension D_{040} of of PP and PP nanocomposites (a) before stretching and (b) after stretching.	69
Figure 3.11 Schematic illustration of crystal structure evolution in biaxially oriented films (MD-ND plane).....	70
Figure 3.12 Mechanical properties of Biaxial Orientated PP and nanocomposite Films (a) Modulus; (b) Strain at break; (c) UTS.	71
Figure 3.13 Elongation to break in TD versus MD in all biaxial oriented films.	72

Figure 3.14 Relative oxygen permeability before and after biaxial stretching.	74
Figure 3.15 Comparison of relative oxygen permeability between experimental and model prediction.	76
Figure 4.1 Stress-strain response of PP and PPNC5 during two stretching modes along different stretching direction: a). along MD in simultaneous stretching; b) along MD in sequential stretching. c). along TD in simultaneous stretching; d) along TD in sequential stretching. Stretching temperature is 156 °C and stretching rate is 200% s ⁻¹ /200% s ⁻¹ along MD/TD in all cases.	88
Figure 4.2 Effect of stretching rate on stress-strain behavior during biaxial stretching of PP and PPNC: a). along MD in simultaneous stretching; b) along TD in simultaneous stretching. c). along MD in sequential stretching; d) along TD in sequential stretching. Stretching temperature is 156 °C in all cases.	91
Figure 4.3 Effect of stretching temperature on stress-strain behavior during simultaneous biaxial stretching of PP and PPNC: a). along MD; b) along TD.	93
Figure 4.4 Optical performance of simultaneously and sequentially stretched film under stretching temperature of 156 °C and MD/TD stretching rate of 200% s ⁻¹ /200% s ⁻¹ , top, microscopy image, (a)BOPPC5_sim(b) BOPPC5_seq; bottom, (c) Total transmittance.	96
Figure 4.5 Thickness profile of biaxially stretched BOPP and BOPPC.	97
Figure 4.6 2D SAXS of extruded and biaxially stretched PP and PPNC.	99
Figure 4.7 1D SAXS intensity profile and long period information of simultaneous and sequential biaxially stretched BOPP and BOPPC. (a) 1D SAXS intensity profile; (b) Long period.	101
Figure 4.8 Tensile properties of simultaneously and sequentially stretched BOPP and BOPPC: (a) tensile modulus; (b) tensile strength; (c) elongation at break.	103
Figure 4.9 Oxygen permeability of simultaneously and equationally stretched BOPP and BOPPC films.	105
Figure 5.1 Unfoamed disk and expanded pp and pp nanocomposite foam.	116
Figure 5.2 SEM micrographs of PP and nanocomposite foam (a) PP-E foam; (b) PPNC3-E foam; (c) PPNC5-E foam; (d) PPNC5B-E foam.	118
Figure 5.3 Cell size distribution of PP and PP nanocomposite foam (a) PP-E foam; (b) PPNC3-E foam; (c) PPNC5-E foam; (d) PPNC5B-E foam.	119
Figure 5.4 Representative TEM micrographs for unformed and foamed PP nanocomposite (a) unfoamed, compression molded PPNC5B; (b) foamed PPNC5B close to a cell edge, “poor” sample; (c) foamed PPNC5B in cell middle, “poor” sample; (d) foamed PPNC5B close to a cell edge at low magnification, good sample ; (e) foamed PPNC5B at higher magnification, good	

sample.	120
Figure 5.5 Uniaxial melt extensional viscosity transients (η^e) at several strain rates for PP and PP nanocomposites.	122
Figure 5.6 Biaxial deformation behavior of PP and PP nanocomposites at different stretch temperature and strain rates (a)150 °C and 50% ⁻¹ ; (b)150 °C and 100% ⁻¹ ; (c)155 °C and 50% ⁻¹ , deformation behavior neat PP 160 °C 50% ⁻¹ of is inserted with arrow.	124
Figure 5.7 Maximum stretching ratio along one direction of PP and PP nanocomposite when subject to biaxial deformation.	125
Figure 5.8 Quasi-static compressive stress–strain curves of EPP foams at about approximately 1 s ⁻¹ (a) loading (b) loading-unloading.	128
Figure 6.1 SEM of fractured cross section of injection molded samples (a) PP (b) TPO1 (c) TPO1-N2 (d) TPO1-S1.	136
Figure 6.2 Contact angle measurements: Top row, PP ; Bottom row, CaCO ₃	138
Figure 6.3 Comparison of 3 representative TPO with selected composition compared to commercial TPO1.	139
Figure 6.4 Photo of TPO nanocomposite R with various thickness, top 1.5mm; bottom, from left to right, 2mm, 3mm, 4mm.	140
Figure 6.5 Transmittance and haze as a function of sample thickness.	141
Figure 7.1 Optical micrographs of top view of sequentially stretched BOPP nanocomposite film with 5wt% loading from continuous production line: (a) 5X lower magnification; (b) 20X higher magnification.	146
Figure 7.2 SEM micrographs of BOPP nanocomposite film from cross-section view: (a) clear film from equal-biaxial simultaneous stretching; (b)(c) voids of different cavitation size in films from asymmetric sequential stretching, the tenter frame production line.	147

Chapter 1. Background

Thermoplastic polymeric materials have been used among numerous applications in both daily life and advanced engineering over the past decades due to their functionality, chemical stability, low cost, lightweight, the easiness of thermal processability and recyclability. Particularly, of these thermoplastic polymers, polypropylene and polypropylene based thermoplastic polyolefin (TPO) played an important role especially for flexible transparent packaging film, lightweight foam, and injection molded automotive parts. These applications demand further improvement in both processing and final property without sacrificing other key parameters to accommodate the development of technology which may not be satisfied by base polymer alone. One method to address these demands is incorporating nanoparticles into polymer matrix to construct polymer nanocomposites (PNC). PNC has attracted significant interests for a long time with overall reinforcement against base polymer due to the synergistic effect and hugely enhanced matrix-filler interfacial interaction. The present research is therefore focused on polypropylene and thermoplastic polyolefin (TPO) based nanocomposites which is divided into three parts based on the different processing techniques aimed for different applications. The primary part of this dissertation (Chapter 3 and 4) is concentrated on biaxially oriented polypropylene nanocomposites for flexible transparent barrier films; the second part of this dissertation (Chapter 5) is about polypropylene nanocomposite foam with high expansion ratio for lightweight application; the third part of this dissertation (Chapter 6) reports a preliminary effort on thermoplastic polyolefin nanocomposites with improved mechanical and optical for injection molded automotive parts. An overview for the primary project will be discussed in this chapter.

1.1 Biaxially oriented polypropylene clay nanocomposites barrier film

1.1.1 Research background and motivation

Transparent packaging barrier film has played an important role our daily life with rising demands in food industry and non-food product such as health care and consumer goods [1]. Generally, transparent barrier packaging film is expected to serve two main purposes: 1. barrier as the most important property as well as mechanical strength protect the packaged items against gases, moisture, aroma, and contamination for extended shelf life; 2. optical transparency meet the rising needs for consumer awareness in food health hygiene and health concerns. The global market size for transparent packaging barrier film was estimated at 9,192.68 million in 2020 and was anticipated to reach 14,872.27 million by 2026 with a compound annual growth rate (CAGR) of 8.34% [2]. The major driven force for this growth is food packaging which contributes more than half share of the global market. To support the growing need for preserving better-quality foods or non-food products with further extended shelf life, packaging film with increasing gas permeation resistance, mechanical robust while maintaining the optical transparency is always desired. In addition, with these efforts, the packaging film manufacturers may replace the usage of aluminum foil to some extent to help with sustainability. It has been recognized that constructing a nanocomposite with nanoparticles could improve barrier properties by creating a tortuous path which will decelerate the movement of gas molecules through the matrix. However, a conflict may exist between required stretchability and added rigidity due to presence of nanoparticle when it comes to biaxial orientation. Therefore, this research is aimed to fabricate biaxially oriented nanocomposite films with enhanced barrier without deterioration of other properties and understand the processing-structure-property relationship.

1.1.2 Biaxial orientation: a general introduction

Most of the transparent barrier packaging films were manufactured via biaxial orientation technique. During this process, a plastic film or sheet is stretched in two perpendicular directions to produce a thinner film. The first direction, also called the machine direction (MD) follow the direction that the initial film or sheet is extruded or rolled. The second direction regarded as transverse direction (TD) refers to the direction that perpendicular to the machine direction but within the same plane of the film. Biaxial stretching is usually semi-solid just below the melting temperature, the high stretching force causes more effective alignment of polymer chains following particular direction and such molecular orientation impart the final film with potentially improved optical transparency, mechanical robustness, gas barrier, birefringence, dielectric properties [3]. These significant improvements which were not attainable compared to conventional uniaxial stretching or sing-step process such as single bubble blown film. In addition to producing packaging film, biaxially orientation process was also widely in other application such as insulation film, transparent film for display, laminated film, labelling film, shrinkable film, dielectric film, and separator film [4–10]. Different processing conditions were applied to suit the end-use.

Based on the deformation pathway, biaxial orientation is classified into two modes: simultaneous and sequential stretching. In simultaneous biaxial orientation, the specimen is drawn along the perpendicular machine direction (MD) and transvers direction (TD) as the same time. The stretching speed and strain ratio are the same due to the nature of the simultaneous process. In contrast, the deformation in sequential biaxial orientation is applied in two stages where during the first stage, the initial specimen is stretched along the machine direction while the width along the transverse direction is kept at constant. At the second stage,

the already MD-stretched specimen is drawn along the TD while the width along MD is kept at constant. The sequential biaxial stretching therefore could be considered as two separate steps of uniaxial stretching with constrained width along perpendicular direction. The temperature, rate and strain during MD stretching and TD stretching could either equals or differs depending on the instrument and purpose.

Biaxial stretching occurs subsequently to a casting or extrusion line in a typical industry manufacturing. There have been three technologies developed to manufacture biaxially oriented films, i.e., tenter frame, double bubble, and biaxial rig stretcher. Tenter frame process has been well-developed as the most common and commercially available process in terms of producing biaxially oriented films. The production line is composed of three components: an extruder, a subsequent roller and a tenter frame. A schematic illustration of the typical setup is shown in Figure 1.1. The extrudate from the sheet die was first stretched uniaxially along MD at the softening temperature by the rotation of a series of chill rolls then it is stretched along TD at elevated temperature on a tenter by movement of tenter grippers or clips. Therefore, typically it is a sequential biaxial orientation process with different temperature set in the rolling and tentering process. It is widely used to fabricate films such as BOPP, BOPE, BOPET, BOPS, BOPLA and BOPTFE [11,12]. The tentered film is usually produced with an unbalanced draw ratio along MD and TD. Such parameters were chosen to manipulate the balance in properties. This continual process has the advantage of being cost effective with high throughput, and the geometry offers the capability to produce multilayer films via coextrusion. However, films produced via tenter has less balanced property and some polymers is not applicable in sequential stretching. The direct contact with chill rolls limits the capability to product optical transparent films. A more mechanically sophisticated tenter frame has been

developed to achieve one-step simultaneous biaxial orientation. It eliminates the chill roller and lessens time cost but introduces more difficulty in adjusting the balance between the stretching direction.

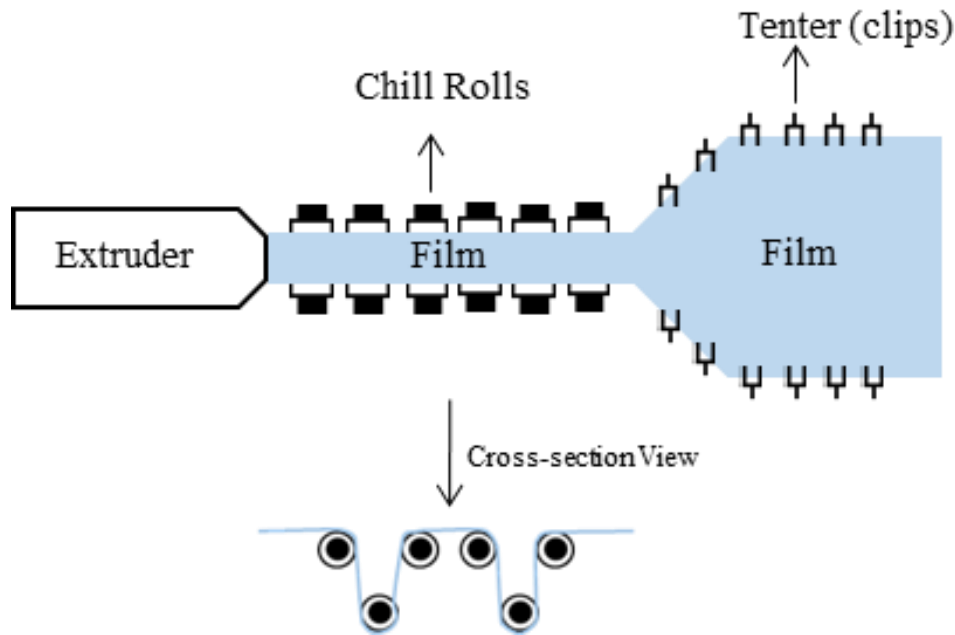


Figure 1.1 Schematic of tenter-frame biaxial orientation process (top view, insert is cross-section view).

The double bubble process has been another widely used technology in industry to produce biaxially oriented films. More often it has found use to produce high shrink films, bags and overwrap packaging for tobacco and CD disks since the double bubble process introduces unique het-shrink property [3,13,14]. It was also be used to produce barrier films. The double bubble production line is vertical setup either downwards or upwards. A schematic illustration of the downwards set up is shown in Figure 1.2 . Melt polymer is extruded through an annular die to form a relatively thick-walled tube inflated by air and quenched in a subsequent water bath. The tube is then collapsed by pinch rolls forming the bottom of the first bubble. Next the tube is reheated through a reheating element to a desired temperature where

the polymer is in rubbery or semi-solid state. The second bubble occurs after the reheating process where the tube is expanded by blowing compressed air to a diameter. Together with the second of the rollers the film is thus stretched in MD and TD. It is a simultaneous orientation since the stretching along the two perpendicular direction occurs at the same time. Usually, the double bubble tubular process fabricates films with more balanced physical property compared with tenter frame [14]. Also, it offers more flexibility in varying the orientation ratio than tenter frame. Compared with single bubble tubular film extrusion, the double bubble process is reported to result in increased crystallinity in polymer films with higher Young's modulus and tensile strength but lower elongation to break [15]. The downside of double bubble process is less control of the temperature and relatively lower manufacturing rates compared with tenter frame.

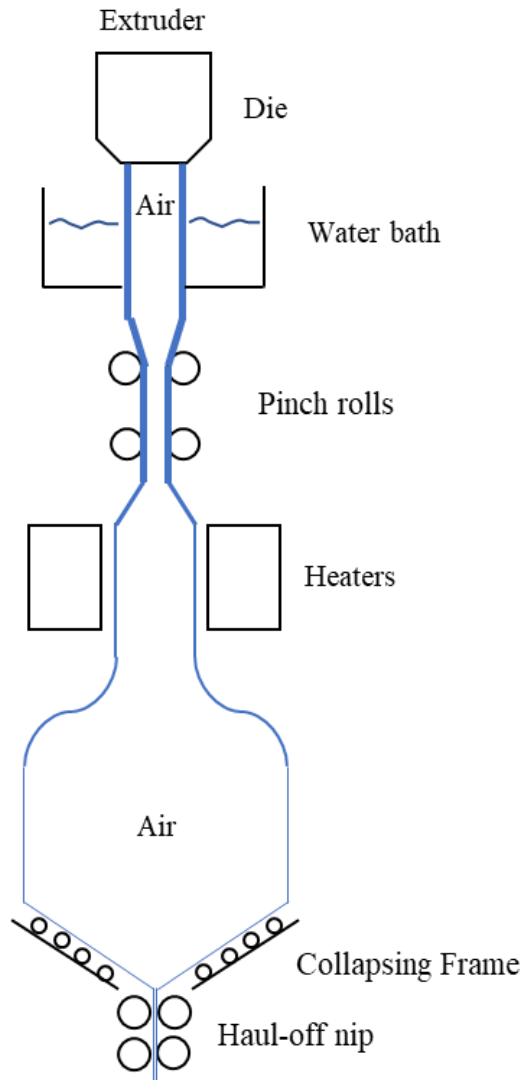


Figure 1.2 Schematic of double bubble process.

The biaxial rig stretcher is the less common of the three techniques. Figure 1.3 depicts the specimen geometry and different stretching pattern in biaxial rig stretcher. In a typical process, the precursor sheet is hold by clamping clips within the stretching unit and suspended in air. The clamping points are uniformly distributed along the four edges and draw the films with controlled profile. Compared with tenter frame and double bubble process which offer high output for industry manufacturing, the biaxial rig stretcher offers: 1. the flexibility for tuning different stretching profile from uniaxial or biaxial stretching, simultaneous or

sequential stretching with controlled stretching rate, oven temperature and stretching ratios; 2. precise measurement via sensors for stretching forces, displacement, oven temperature, clip temperature and sample surface temperature. Due to these benefits, the biaxial rig stretcher is more often utilized as a pilot-line production to evaluate processing conditions and films recipes. Development of the biaxial rig stretching instrument for pilot line and laboratory study has therefore driven huge interests as such enables the fundamental study of processing-structure-property relationship in biaxially orientated polymer films [16–21]. Moreover, it could be used not only for simulation of the tenter frame and double bubble process, but also for modelling of the biaxial deformation behavior occurred in free surface molding process such as thermoforming and injection stretch blowing molding where tradition monoaxial stretching simulation are inadequate [16]. The latter has particular significance as the biaxial deformation varies extensively at different processing stages and parts location in these processes where traditional modelling lacks accuracy. Furthermore, to investigate the structure development of uniaxially and biaxially oriented films, the in-situ observation capability, besides the stress-strain recording, such as birefringence, light scattering, small angle X-ray scattering (SAXS) during the stretching process developed.

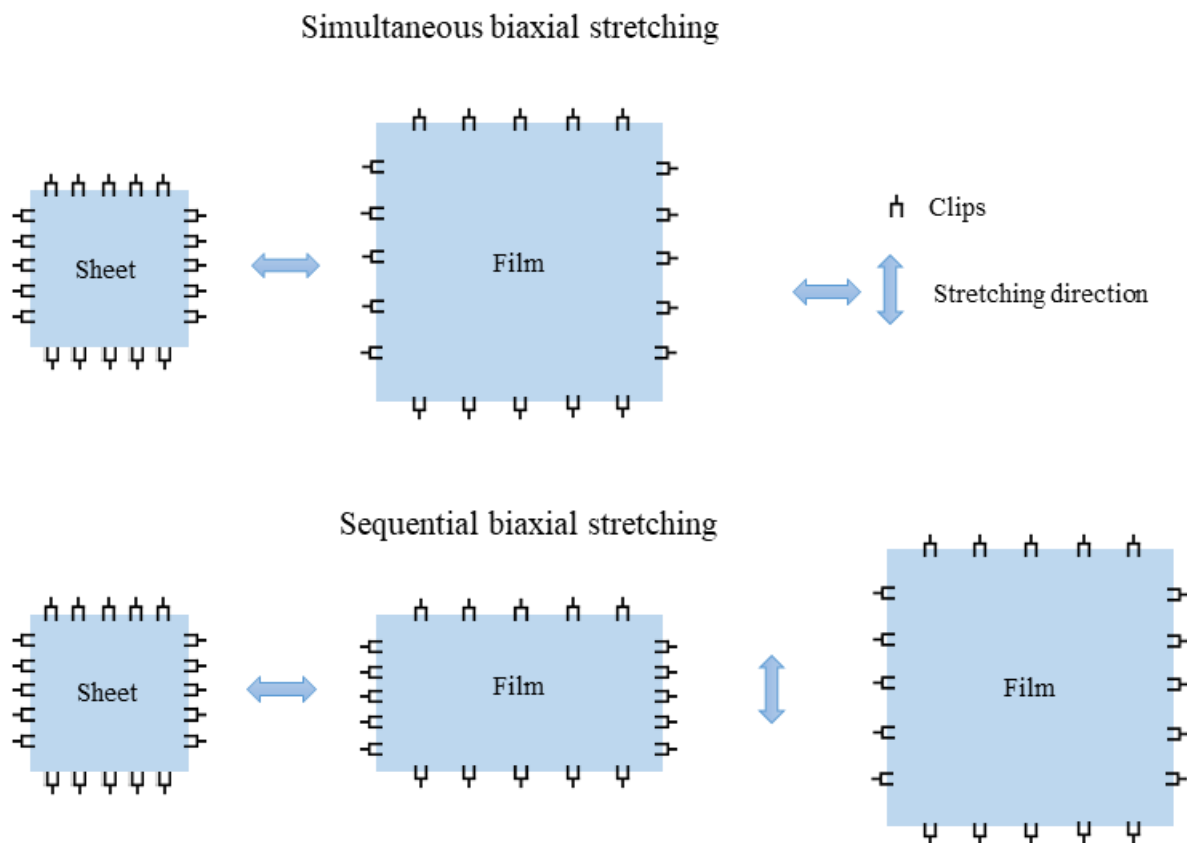


Figure 1.3 Schematic of biaxial rigs and two stretching modes.

In addition, the biaxial rig stretcher together with double bubble process was used to produce simultaneous biaxially stretched polymer films that is not tolerate in sequentially stretching such as EVOH [22]. This is because the crystallization rate of EVOH is too fast during the first stretching step which makes it unapplicable to be oriented in the second direction. Other application involves the ability to product optically transparent films for liquid crystal display panel benefiting from suspension of the precursor sheets in air eliminating the direct contact with the machine [8,20]. The limitation of this technique is associated with the system complex and high maintenance cost since a lot of moving parts is involved.

In this research, the biaxial rig stretcher, a Karo IV laboratory stretcher from Brückner, has been selected to produce biaxially stretched nanocomposite films under well-controlled

stretching rate and temperature [12]. The processing, structure, and property of the biaxially oriented nanocomposite films were investigated. The films obtained via this laboratory rig stretcher was also compared with films of the same composition manufactured from a tenter frame production line.

1.1.3 Biaxially oriented polypropylene (BOPP): processing and structure development

Biaxially oriented polymer films has gained its success since 1950's [20] whereby polypropylene is one of the largest segment in this category. This is because of its low density, high temperature service window, good mechanical, and low cost compared to other common biaxially oriented polymers. Other advantages of BOPP include high clarity and gloss, non-toxicity, wide service temperature window, resistance to oils and greases, good barrier to water vapor, good puncture, high tensile strength, high dielectric breakdown and dimension stability with environmental changes [3]. These advantages endow BOPP with a broad application.

The molecular structure in PP has been well established over the past decades in terms of molecular tacticity, crystalline and amorphous morphology, and structure evolution. Depending on the relative position of methyl group on the carbon backbone, polypropylene can exist with three forms with different tacticity, i.e., isotactic, syndiotactic and static. Isotactic polypropylene homopolymer has overall the highest crystallinity and is also the most commercially available. Typical polypropylene is synthesized using traditional Ziegler–Natta catalysts and has a polydispersity of about 8-12 [3] while more recently polypropylene with very narrow molecular weight distribution synthesized using metallocene-type catalysts which are usually consider to possess improved physical properties.

As semicrystalline polymer, the molecular chains isotactic polypropylene homopolymer could take helical confirmation and form monoclinic α -form, hexagonal β -form,

or orthorhombic γ -form crystalline structure under different processing conditions [23]. Among these, α -form crystal is the most stable form with a monoclinic unit cell and adjusted orthogonal crystal axis a^* , b and c . The crystalline region of compression molded or extruded PP at low stress state is dominated by the isotropic configuration consisted of spherulites with radial and tangential lamellae surrounded by amorphous region. On the other hand, external stretching could originate a stacked lamellar structure or even fibrillar crystalline morphology at high strain.

Due to the large segment size of BOPP, there have been numerous efforts to understand the processing, structure development and properties associated with the biaxial orientation process. The effect of PP in precursor sheet as well as change in processing parameters are considered to affect the processing behavior and thus the formed structure. In terms of processing behavior, the structure in precursor prior to biaxial stretching played an important role in BOPP processing and efforts were made to improve the stretchability and tensilizing BOPP film. Usually, it was considered the melt flow index (MFI) has a direct effect on the processability of polypropylene during biaxial stretching. The higher the MFI, the easier for the film to be orientated. The crystalline state of the polypropylene was also considered to control the stretching features. Previous study indicated the sheet with higher crystallinity was more difficult to orient [24,25]. An approach to develop a polypropylene material having a higher crystallinity and good processability was proposed by blending polypropylene homopolymers with ethylene/propylene copolymers. Capt et al. [26] also reported that the biaxial stretching behavior will be dependent on both the crystallinity and crystallite size. In another work, Bullock and Cox [27] studied the stretching process of polypropylene with higher tacticity and crystalline order. A correlation was proposed between the resin tacticity

and the film orientability during biaxial stretching.

Tamura et al. [28] investigated the effect of molecular structure on stretchability for sequential biaxially oriented polypropylene film on a tenter. By verifying the thickness uniformity of BOPP, the researchers found that low crystallinity and wide molecular weight distribution were effective in improving the stretchability. Reducing the crystallinity also helps widening the process temperature window in the stretching process. In continued work, they reported that blending of low modulus polypropylene (LMPP) to PP was effective [29]. The ternary blend could be stretched up to an MD stretching ratio of 12 without film breakage whereas the conventional BOPP film could be stretched only 6 times in the MD. It was speculated that LMPP blends reduced the spherulite size, increased the amorphous phase in the lamella thickness without changing crystal phase thickness, decreased the crystallization speed, and thus reduced the yield values during the stretching process and increased the stress buildup ratio. As a result, they improved film thickness uniformity of biaxially stretched film and reduced film break during the production line. Overall, it is expected to tune the processing behavior to produce uniform BOPP films with desired properties by modifying the molecular structure, e.g., tacticity, crystallinity, molecular weight, molecular weight distribution.

In addition to molecular structure, change in the processing parameters can also influence the processing behavior and thus structural development in biaxial stretching and therefore the final properties. The major variable process parameters involved in biaxial orientation process include deformation mode, stretching temperature, and strain rate and final stretch ratio. It is as expected that strain rate will affect the processing behavior in biaxial stretching. A study found that stress-strain response of polypropylene undergoes a shift from the ductile to the quasi-rubber-like after high strain rates over 750mm/s [24]. Moreover,

increasing strain rate also helps increase the homogeneity of the deformation process and thus the film. In another work by Kamal and coworkers[18], the strain rate in simultaneous biaxial stretching was found to have a large influence on biaxial deformation homogeneity. It was also found that homogeneous biaxial deformation was achieved if the Hencky strain rate was higher than 0.1 s^{-1} at temperatures 15°C to 5°C below the melting point. A linear correlation was found between the nominal biaxial yield stresses and temperature in the range under investigation.

Compared with strain rate, the stretching temperature appeared to be the more dominating parameter [30]. One reason for this is that the degree of undercooling, i.e. the difference between melting temperature and processing temperature, determines the phase composition of the polymer before stretching [31]. In a comparative work between biaxial orientation behavior of polypropylene, polyethylene terephthalate (PET) and high impact polystyrene (HIPS), PP was found to draw the highest stress and is the most temperature-sensitive of the materials [16]. By reducing the temperature from 165°C to 155°C , the stress drawn for a given strain in PP falls to approximately a quarter of its original value. Rettenberger et al. [24] investigated the effect of temperature on the stress-strain behavior during stretching of polypropylene near the melting point. They found that in the temperature range of $140\text{--}160^{\circ}\text{C}$ the tensile behavior of polypropylene undergoes a shift from the ductile to the quasi-rubber-like deformation behavior. A typical ductile behavior with a yielding, neck propagation, and strain hardening was observed up to 155°C . At higher temperatures, the deformation response was a quasi-rubber-like with an absence of yielding. Similar results were also confirmed by Capt et al. [26] Yang and co-workers [32] studied the general stress-induced crystallization behavior of the BOPP. They found that at high temperatures, the stretching ratio

greatly influenced the obtained crystalline structure. that a clear trend with an increasing tensile ratio. The crystallinity increased by an average of 20% after MD stretching. A trend of increase T_m , ΔH_f , ω_c and congruently decreased ΔT at lower strain was observed but the trend was not so clear at high strain rate. They also confirmed that β crystal did not form during the entire MD hot-stretching process.

The deformation mode, i.e., sequential stretching and simultaneous stretching depending on the stretching sequence, is another important parameter. The former could be considered as combination of two steps of uniaxial stretching with constant width. A comparative work between constant width, simultaneous biaxial stretching, sequential biaxial stretching revealed that simultaneous biaxial stretching draws higher stress at given strain compared with uniaxial stretching at constant width as well as the first stretching step in sequential stretching (the latter two is essentially the same) [16]. On the contrary, the stress level during second step in sequential stretching was higher than simultaneous biaxial stretching. Lin et al. [33] also demonstrated the two stretching behavior with different target strain.

The structural development in biaxial stretched films has been extensively studied[33–37]. It is generally accepted that while sharing some similarities with uniaxial stretching, biaxial stretching differs from the two orthogonal drawing forces leading to characteristic structure development. In some studies the researchers compared the simultaneous biaxial stretching from uniaxial stretching, and they have drawn similar conclusion that polymer chains tend to more oriented in the plane of the film during simultaneous stretching while the due to the nature of two orthogonal stretching force[35,38,39]. The high stretching force and high area stretching ratio causes higher degree of polymer chains alignment and introduces

significant improvements which were not attainable in uniaxial stretching. After high stretching ratio, the initial crystalline morphology before stretching will transform to fibrillar structure after stretching [35].

The comparison between simultaneous biaxial stretching and sequential biaxial stretching has been the topic of many studies more recently thanks to the advancement of biaxial orientation testers. Uejo and Hoshino [35] investigated the structure of biaxially stretched polypropylene film in detail by means of x-ray pole figure, birefringence and electron microscope. Three kinds of crystal orientation during biaxial orientation were confirmed: 1) c-axis along the stretching direction; 2) b-axis normal to the plane of the film; 3) [110] vector weakly normal to the film. They proposed a deformation model by assuming the hot-pressed film is composed of woven structures. In free uniaxial stretching, the woven structural element was oriented randomly around elongation axis. While in both uniaxial stretching with constant width and biaxial orientation, the structural element was oriented parallel to the plane of the film with crystal b-axis oriented perpendicular to the plane of the film. They also found that in sequential stretching, the fibrillar structure is oriented comparatively parallel to the stretching direction which differs from simultaneous stretching where a random orientation was suggested. Nitta et al. [36] developed an in-situ measurement of molecular orientation of biaxially stretched films not in three dimension, i.e. not only in plane but also in thickness direction. The findings about difference between sequential biaxial stretching and simultaneous biaxial stretching was similar. In the former, the lamellar cluster blocks were orientated along first stretching direction and then rotated to the second stretching direction. This differs from simultaneous biaxial stretching, where the crystalline lamellae rotate toward an in-plane alignment.

1.1.4 Barrier in biaxially oriented polypropylene (BOPP)

The structure and property relationships of biaxially orientated film has been widely studied. The part particularly focuses on the barrier performance of BOPP. Penetration of gas molecules through a polymer thin film is a complicate process involving gas absorption, dissolution, diffusion, and desorption. To characterize this phenomenon, permeability coefficient, P is introduced and expressed as:

$$P = D * S \quad (1.1)$$

Where D is the diffusion coefficient and S is the sorption coefficient or solubility. It was generally recognized that biaxial stretching improves the gas barrier performance by controlling the orientation and crystallinity. In amorphous polymer only orientation occurs via ordered region while in semicrystalline polymer both crystallization and orientation occur via packing and alignment of chains. The consensus is that diffusing molecules are primarily in the amorphous region or free volume while the crystalline region or highly order regions is considered as improbability obstacles. Stretching leads to an increase in crystallinity which means a reduction in the amorphous volume faction and thus a reduction in solubility. The orientation and morphological change of crystallite will also impede the diffusion path of gas molecule. Furthermore, a reduction in amorphous chain mobility is also expect after polymer chains being starched and thus the difficult of diffusing, i.e., diffusivity will also decrease.

There have been a number of efforts try to predict the barrier performance by understanding the correlation between structure and permeation rates of biaxially oriented films [40–45]. Conner and Schertz [40] investigated the effect of density and permeability of different gaseous species after drawing process. They found that influences of crystallinity and molecular orientation on permeability follows the concept that crystallinity reduces

permeability. This is due to 1) a reduction in the volume fraction of penetrable amorphous region; 2) an increase in the diffusion path by impenetrable barriers, presumably crystallites; and 3) a reduction in segmental motion within the amorphous volume. Furthermore, by analyzing the effect of molecular diameter on diffusion rate they showed that amorphous mobility in polypropylene lower than that in natural rubber. Ward and co-workers[46] also studied the diffusion of oxygen in both uniaxially and biaxially stretched polypropylene. With few exceptions the permeability coefficient decreases upon drawing although the effects are small, particularly in the case where the coefficient does not fall below about 60% of the isotropic value. The molecular orientation, as indicated by refractive index measurements is considered as a major cause of the reduced permeability.

Lin et al. [33,41] investigated into the relationship between biaxial orientation and oxygen permeability of polypropylene. Although they confirmed the reduction in the oxygen permeability in the biaxially stretched film compared to unstretched, surprisingly, the reduction did not correlate with the amount of orientation as measured by birefringence or with the fraction of amorphous phase as determined by density. No consistent relationship was neither observed between the oxygen permeability and the thermal history of the precursor sheet. Instead, the decrease in permeability was attributed to reduced mobility of amorphous tie molecules as measured by the intensity of the dynamic mechanical β -relaxation. A one-to-one correlation between the oxygen permeability of BOPP films and the mobility of amorphous tie chains was established. In addition, they also indicated the chain mobility in the stretched direction was dependent on the final stress during biaxial stretching.

Coleman and co-workers [43] probed the effect of crystallinity, chain dynamics and free volume on barrier properties of biaxially oriented semicrystalline films in detail. A three-

phase structure containing rigid amorphous phase, mobile amorphous phase, and crystalline phase was elaborated as characterized by DSC and PALS. It is indicated that the free volume of amorphous fraction is decreased as well as the activation energy of relaxation. They concluded that the reduction in permeability coefficient was mainly due to reduction in diffusivity and the reduction dependency on gas molecule size indicated a change in the free volume distribution upon strain-induced crystallization.

On the other hand, improving the oxygen barrier performance has always been demanding to support the growing need for preserving better-quality foods or non-food products with further extended shelf life and reduce the usage such as aluminum foil to help with sustainability. Indeed, the necessity of developing high barrier polymer systems has given rise to various efforts to further improve barrier property of biaxially oriented films such as multilayer coextrusion, blending [47], copolymerization [48], surface coating [49] and metallization [4,50–55]. However, these methods are associated with increased instrumental complexity, volatile organic solvents, and high energy consumption. Alternatively, recent developments in polymer nanocomposite incorporating nanoparticles appears to be a more cost-effective method to achieve this goal. Addition of low concentration of nanofillers improved barrier performance by creating a tortuous path which will decelerate the movement of gas molecules through the matrix. A number of studies have demonstrated such effect which will be discussed in the later section.

1.1.5 Polymer nanocomposite

Polymer nanocomposites refer to a class of hybrid materials consisting organic polymer matrix and dispersed inorganic/organic nanoparticle filler which at least has one dimension of nanoscale ($<1\mu\text{m}$). Due to the fact that they exhibited remarkable improvements

of material properties compared to base polymer, there have been made tremendous developments in this nanotechnology field. On one hand, this enhancement of polymer nanocomposites relative to virgin polymer originated from synergistic effect by combining merits of polymer matrix and nanofillers. The advantage of polymer matrix includes such as ease of processing, flexibility, corrosion resistance, light weight and low cost while the filler has a reinforcing effect and impart functionality such as rigidity, impermeability, selectivity, thermal stability, thermal conductivity, wear resistance, flame retardancy, dielectric property [56–58]. On the other hand, more importantly, compared with conventional macro-composites or micro-composites, the enhancement in nanocomposites can be tremendous due to large interfacial area between nanofiller and matrix and this allows the property reinforcement to be achieved at relatively low filler loadings which helps with maintaining some of the matrix property. As a result, polymer nanocomposites have found broad application including construction, electronics, appliances, packaging, automotive, and aerospace.

Nanoparticles can be broadly divided into various categories depending on their morphology, size, physical and chemical properties [59]. Considering the overall geometry, the nanoparticles can be classified into 0D (ultra-small particles, quantum dots), 1D (fibers, whiskers), 2D (platelets, sheets) and 3D (spheres or tubes) [60]. 2-dimensional nanoparticles, or considered as nanosheet or nanoplatelets, possess a geometry with two dimensions outside of the nanometric size and one nanometer or even atomic dimension in thickness. Particularly, the geometry nature has endowed the 2D nanofillers ideal for barrier improvement [61]. Considerable research has been done focused on incorporation of 2D nanomaterials to construct polymer based nanocomposites [62]. Various 2D platelet-like nanoparticle have been prepared including layered silicate [57], graphene [63], metal phosphates and phosphonates

[64], hexagonal boron nitride [65], metal organic framework [66].

Among these 2D nanofillers, layered silicate, or clay, has been the most popular material. This is mainly due to its high modulus, increased barrier, low cost, heat resistance, large surface area, availability and ease to melt mix with polymers [57]. High aspect ratio of clay nanoplatelet induces dramatic change on morphology, structure, chain dynamics, and properties in polymer matrix even at a relative low concentration. Since the pioneering research done by Toyota on nylon/clay nanocomposites [67,68], polymer layered silicates nanocomposites have attracted massive interests in both academia and industry. Montmorillonite (MMT) is one of the most common layered silicates used in polymer nanocomposites belongs to the structural family called 2:1 phyllosilicates. Their crystal structure consists two-dimensional layers made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. The thickness of one layer is approximately 1 nm and its typical lateral dimensions can vary from 30nm to several microns or larger with typical value of 100-200nm. This results in a particularly high aspect ratio. The silicate layers can be weakly bounded by relative weak dipolar and van der Waals forces and have the tendency to stack together as tactoids. In addition, the interlayer spacing, also called galleries, is filled with alkali and earth alkaline cations, which counterbalance negative charges within the layers generated by isomorphic substitution (Al^{3+} replaced by Mg^{2+} or Fe^{2+} , or Mg^{2+} replaced by Li^{1+}). Typical gallery spacing is around 1 nm for dehydrated Na^+ montmorillonite. Layered silicates possess two indispensable characteristic: their layered structure allows them to be delaminated into thinner layers or even exfoliated into platelets and their chemical nature allows them to be modified through ion exchange reactions with organic and inorganic ions[57][69][70]. When it comes

to hydrophobic polymers such as polyolefin, due to the inherent incompatibility between polar clay and non-polar polymer matrix, an ion-exchange reactions with cationic surfactants including primary, secondary, tertiary, and quaternary alkylammonium or alkyl phosphonium cations to fabricate organically modified clay.

It has been recognized the properties of polymer-layered silicate nanocomposite depend on the state of nanoclay dispersion in the polymer matrix. In general, the morphology in such systems can be classified into three different states: 1) intercalation, where polymer chains enter into a layered silicate structure expanding the galleries, but the ordered structure is still maintained, 2) flocculation, where intercalated and stacked silicate layers flocculated to some extent due to the hydroxylated edge-edge interactions, 3) exfoliation, where each individual silicate layers are separated by polymer chains. Exfoliation is considered as the most desirable condition to achieve the most significant reinforcement. Some researchers also added the agglomeration as the fourth type.

Dispersion and delamination, and even exfoliation of layered structure retain a significant challenge to scale up the fabrication of these materials. Furthermore, they tend to agglomerate due to their high surface energy when mixing with polymer matrix. Various methods have been developed to address this issue: solvent mixing [71], in-situ polymerization [72,73], and melt blending method [74–78]. The former two methods can be associated with increased complexity, volatility, solvents or monomers waste, and re-agglomeration after removing the solvent. Thus, of these methods melt blending intercalation appears to be the most common and feasible method for the preparation of polymer clay nanocomposites in industry due to its low cost, simplicity and being environmental-friendly. The mechanism of melt intercalation compounding method has been described as a “peeling off” mechanism[79].

Under shear stress, the clay tactoids or stacks are broken apart and become smaller ones or single tactoid. Further the clay nanolayers are broken apart from each other into potential single layers when exfoliation force exceeds the attractive force between adjacent layers. Meanwhile polymer can penetrate into the galleries interlayer creating a peeling angle that benefits the transfer of shear stress. Processing parameters such as shear force, temperature, and residence time determine the resulting composites and thus the properties.

Due to the inherent incompatibility between hydrophobicity and hydrophilicity, extensive efforts were to improve the interaction between polymer matrix and fillers via melt mixing. One approach is to introduce compatibilizer to increase the miscibility of nonpolar polymer matrix between PP with to obtain polymer clay nanocomposites with desirable structure. Maleic anhydride grafted polypropylene (PP-g-MA) appears to be more effective compared with other compatibilizer such as amine functionalized PP (PP-g-NH₂) [80,81]. Multiply factors including maleic anhydride content, the compatibilizer to clay ratio, and the molecular weight were reported to have an influences on the compatibilizing effect between polymer and clay and thus the delamination and exfoliation state in nanocomposites [82–84]. An optimized compatibilizer content should be determined to achieve the described miscibility and good dispersion.

Modification and functionalization of clay nanoparticles has been another important approach. As describe above, an ion-exchange reactions with cationic surfactants prepare organoclay has been widely adopted. The length of alkyl tails is reported to be one factor affecting the exfoliation of nanoclay [85]. The long organic chains of such surfactants with positively charged ends are tethered to the surface of the negatively charged silicate layers, thus expanding the gallery spacing. Kim et al. [77] prepared a series of hybrids of maleic

anhydride grafted polypropylene with unmodified or modified clay (Na-MMT or DDA-MMT). They showed that with a cationic-surfactant (dimethyldioctadecylammonium chloride) modified clay, the nanocomposite showed a good dispersion of exfoliated silicates in the polymer matrix while in composite with unmodified clay hybrid, a macro phase-separated mixture was formed instead of intercalation. In addition to ion exchange, pre-treating the organically with silane coupling agent prior to melt mixing has been shown to further improve the interaction between polymer matrix and clay nanoparticles by attaching to two interface sites: either at the edges or at the faces [86–88]. Reactive silane coupling agent can replace the relatively weak force of polymer-particle attraction with stronger chemical bonds. Furthermore, by doing so, the usage of compatibilizer could be reduced which will benefit processing and properties under certain circumstances since the viscosity of the compatibilizer is usually much lower than the polyolefin matrix.

Recently, our group has reported a strategy to achieve enhanced interfacial interaction via a masterbatch method incorporating solvent-free vapor phase silane-treated organoclay coupled to high-molecular weight functionalized PPgMA compatibilizer [74,75,89]. The vapor phase treatment provides enhanced silane penetration into the interlayer galleries compared to solvent based. The reactive coupling occurring at both faces and edges of silicate layers allows significantly enhanced interfacial adhesion and improved nanoparticle dispersion. Improved rheological behavior in the form of greater melt straining hardening during extension flow, which are indispensable for processing, promotes nanocomposite processability in foaming and blown film application, which shed further light in the potential for biaxially stretched film process.

1.1.6 Polymer nanocomposite for improved barrier

As stated above, incorporating 2D nanoplatelets with large aspect ratio such as clay layered silicate has been attracted great interest due to their geometry nature in reducing gas permeability in polymers by impeding the diffusion of oxygen and other small molecules [61]. These nanoparticles are impermeable to gases and thus forcing gas molecules to by-pass these nano-obstacles to follow a more tortuous pathway of diffusion. Figure 1.4 depicts an ideal case where orthogonally shaped platelet particles of uniform size were evenly dispersed and arrayed in parallel pattern perpendicular to the diffusion direction. Due to impenetrability of these particles, diffusing species are forced to take longer transportation distance.

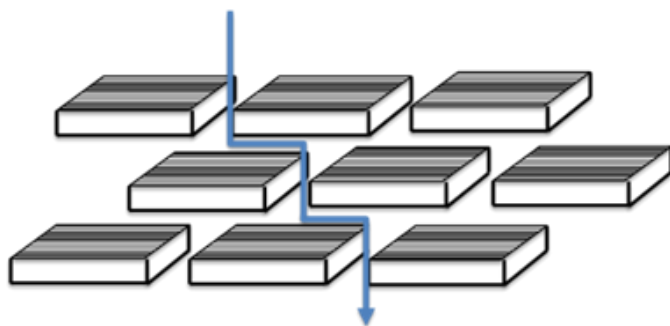


Figure 1.4 Tortuous diffusion pathway created by parallel arranged uniform rectangular platelets.

The permeability of a polymer clay nanocomposite system depends on the filler content, aspect ratio, the degree orientation and dispersion of the silicate layers. Nielsen [90] derived a simple model regarding permeation phenomenon of gases through a platelet-shaped particle reinforced polymer by calculating tortuosity, i.e. the increased diffusing length. It is assumed uniform and parallel arrangement of impermeable 2D barriers were orientated perpendicular to gas diffusion direction.

$$\frac{P}{P_0} = \frac{1 - \phi}{1 + 2\alpha \phi} \quad (1.2)$$

where $\alpha = L/W$ is the aspect ratio of platelets and ϕ is filler volume fraction. This relation shows that as the fraction and aspect ratio of filler increases, the permeability decreases. Nielson model provides reliable estimation of permeability in practice especially in cases at lower loading of nanofiller. Baer and co-workers also showed that Nielsen's model well described the reduction in permeability considering fillers as well as crystallinity [91]. At high loading, particles tend to aggregate where Nielson model may not withstand. Furthermore, compared with other factors a high aspect ratio is more desired factor in maximizing tortuosity.

A number of research has focused on polymer clay nanocomposite as an attractive candidate for improved barrier performance. Pannirselvam et al. [92] reported 30% reduction in oxygen permeability polypropylene-polyether treated clay nanocomposite. Osman et al. [93] showed that oxygen permeability in HDPE-organomontmorillonite (OMMT) nanocomposite with 4 vol% loading was reduced by 40% compared to unfilled matrix. Bunekar et al. [76] prepared PP-clay nanocomposite with sol-gel modified exfoliated and maleated polypropylene via a micro-compounding process and achieved a factor of 14.1 in gas barrier properties at 3 atm in composite over pure PP with. This is attributed to intercalated and partially exfoliated nanocomposite morphology as confirmed from XRD and TEM analysis. Baniasadi and co-workers [94] also showed in significant reduction of permeability in polypropylene clay nanocomposites with up to 5% loading (PPCNC) via in situ polymerization using bisupported Ziegler-Natta catalyst. The composites illustrate intercalation and exfoliation of the clay layers. Villaluenga et al. [95] studied the gas transport in polypropylene clay composite membranes. They found the decrease permeability in filler PP compared to unfilled. The mechanism for the reduction varies such as for helium, diffusion rather than solubility was responsible while

for nitrogen and oxygen, both diffusivity and solubility were reduced by the presence of fillers. To conclude, all these studies have indicated the importance of uniform dispersion with intercalated or even exfoliated layered silicate, and the good adhesion between polypropylene matrix and silicate layers. The decrease in permeability is due to both the retarded diffusion by tortuous path and reduced molecular mobility due to the presence of fillers. The solubility may also be affected.

However, in a study conducted by Bousmina and co-workers [96], the barrier performance to different diffusing species including gases, moisture, and organic vapors was tested. They found that in general the unmodified PP exhibits fairly better barrier performance than its hybrids with PP-g-MA and/or OMMT with exception that an improvement was achieved for the helium barrier properties in the hybrids. This unexpected detrimental effect in barrier to water vapor or methanol is ascribed to the interaction between the gas molecules and the inherent hydrophilicity of clay or the quaternary ammonium salt surfactant and the more polar compatibilizer. They recommended difference such as alternative type of clay, extended annealing to enhance the polymer chain arrangement and reduce free volume in order to improve the composite barrier performance. This work specifies the attention on the potential different effect of compatibilizer and layered silicate depending on specific diffusing molecules.

1.1.7 Biaxially oriented nanocomposite film

Incorporating nanoparticles into biaxially oriented films has been a challenge. There is constrain in application of nanoclay when it comes to biaxial orientation. On one hand, in a typical biaxial orientation manufacturing, the preform is subjected to a high deformation ratio (such as 6×6 in simultaneous BOPP [3]) which is critical as such endows the base polymer

with enhanced mechanical and barrier. High stress and narrow temperature sensitivity was encountered during this rapid biaxial deformation especially for BOPP which is known to draw highest stress compared to other common polymers for biaxial orientation [16]. The increased production demand for high production speed even further aided the high stress tendency. On the other hand, the presence of rigid nanoparticles may have a detrimental effect on ductility and stretchability due to their inherent incompatibility, heterogeneity, and local stress concentration effect. Such conflicts in biaxial orientation process may lead to debonding between filler and matrix. As a result, undesirable cavitation or early breakage occurs which limit the stretching ratio or even decrease the barrier in the final film [97,98]. Moreover, the presence of cavitation or aggregates will act as light scatter which lead to dramatic loss in transparency, which is undesirable in transparent packaging. The potential to such detrimental effect could be more significant with increasing concentration of clay nanoparticles as the potential to form aggregates is higher [99,100].

Due to the conflicts as stated above, there has been limited work reported on biaxially orientated polymer clay nanocomposite film especially polypropylene-clay nanocomposite film. Either a constrained area stretching ratio was used which fell short of practical industrial condition, or some researchers were actually incorporating the nanoclay within a coating layer instead of into the matrix or core layer [101]. Moreover, a significant portion of reported work on biaxially oriented polymer nanocomposite serves the purpose by incorporating these nanoparticles is to introduce cavitation for porous film application [102], which is another actually another scope of topic. Within these limited studies that comply with our research interests of biaxially oriented polymer clay nanocomposite films for improved barrier, there is lack of comprehensive study covering the processing, crystal structure, nanoclay dispersion,

properties as well as the structure-property relation. Some of these studies are summarized as below.

Abu-Zurayk [103] et al. investigated the biaxial deformation behavior and mechanical properties of polypropylene nanocomposite melt blended with 5wt% montmorillonite clay. They demonstrated that the presence of clay increases the yield stress relative to the unfilled PP at typical processing temperatures and that the sensitivity of the yield stress to temperature is greater for pp nanocomposite. The stretching process is also found to have a significant effect on the delamination and alignment of clay particles and on yield stress and elongation at break of the stretched sheet. The maximum area stretch ratio was 3.5×3.5 as indicated in their work.

Tabatabaei and Ajji [39] compared the microstructure and orientation of uniaxially and biaxially oriented PLA and PP nanoclay composite. They have observed intercalation of the silicate layers for the PLA nanocomposite films but neither intercalation nor exfoliation were observed for the PP nanocomposite films. They also found that the crystallite unit cell alignments are appreciably dependent on uniaxial and biaxial stretching and the incorporation of clay influenced the orientation of the crystal unit cell axes (a, b, and c) of the oriented films to some extent. The area stretching ratio was 4×4 for biaxially stretched films in this work.

Rajeev et al.[104] studied the effect of equi-biaxial stretching on the exfoliation of nanoclay in polyethylene terephthalate (PET). They have observed that stretching improved the exfoliation of nanoclay as the concentration of thinner tactoids, longer tactoids and tactoids having higher aspect ratio in the matrix increased due to stretching. They assumed such increase was due to the slippage of the platelets while stretching. Equi-biaxial stretching also imparted preferential orientation of the tactoids in the matrix. It was found that stretch ratio

affected the nanocomposite properties as increase in stretch ratio improved the exfoliation of clay platelets. The dynamic mechanical change and barrier enhancement also confirmed the presence of exfoliated clay platelets in the PET matrix. However, The change of crystalline structure the polymer remained further investigation.

Garofalo et al [105]. investigated the effect of biaxial drawing on morphology and properties of copolyimide nanocomposites produced by film blowing. They successfully produced copolyimide-based nanocomposite blown films in a wide range of stretching conditions which is attributed to higher values of transient extensional viscosity and melt strength of the nanocomposites. The hybrid films showed improved barrier and mechanical properties compared to the unfilled systems and this was inferred owing to the good dispersion and preferential orientation parallel to the film surface, of the silicate platelets.

Shayanipour and Bagheri [54] examined different blend, compatibilizers and organoclays to minimize oxygen permeability of BOPP films. They have found PP film blended with PVA and modified organoclay have lowest oxygen transfer rate ($300\text{cc}\cdot 20\mu\text{m}/\text{m}^2\cdot 24\text{h}\cdot \text{atm}$). The synergistic effect leads to a significant barrier improvement in comparison with conventional methodologies. However, they did not show the details for biaxial orientation and thus the area stretching ratio for BOPP was unclear. Also, the contribution on the barrier improvement from PVA and clay need to be further clarified.

1.1.8 Research Objective and Hypotheses

This research is motivated by the demand to further improve the barrier performance of BOPP film without sacrificing transparency and mechanical strength. Given the lack of studies in biaxially oriented polymer nanocomposite, the objective of this research was to probe the feasibility in fabricating biaxially oriented polypropylene clay nanocomposite films

to practical industry area stretching ratio by incorporating nanoclay additive using the strategy developed in our group. Moreover, the effect of nanoclay on processing behavior, structure and property in BOPPNC films is to be investigated.

Specifically, the hypotheses include:

- 1) Nanoclay in our masterbatch stays well dispersed during biaxial stretching and orientation and allows us to maintain the area stretch ratio as well as transparency of the film.
- 2) The presence of nanolayers will alter the crystalline rearrangement during biaxial stretching.

Chapter 2. Materials and Experimental Procedures

2.1 Materials

Two grades of polypropylene were used for the BOPP nanocomposite film project: PP526P supplied by Sabic, (MFI 8.0, ASTM 1238; density=0.90 g/cm³); PP4792E1 supplied by Exxon Mobile, (MFI 2.0, ASTM 1238; density=0.90 g/cm³). The latter was also used for nanocomposite foam work. The two polypropylenes have a melting temperature of ~165°C. The maleic anhydride-grafted PP (PPgMA) compatibilizer grade was Exxelor PO-1015 supplied by ExxonMobil, which is a random copolymer with ethylene (M_w = 123,000; 0.42wt% bound maleic anhydride). Organically modified montmorillonite Nanomer I.44P was obtained from Nanocor, which has a quaternary ammonium ion surfactant with two octadecyl tails. The reactive silane coupling agent was Dynasylan 1411, an aminoalkyl dimethoxysilane from Evonik.

For the translucent thermoplastic polyolefin (TPO) research, a commercial grade of thermoplastic polyolefin (TPO) used in this research as a reference material: Hifax 7430P (MFI 18.0, ASTM 1238; density=0.91 g/cm³), supplied by LyondellBasell, a UV-stabilized, paintable, unfilled thermoplastic elastomeric olefin (TEO) typically used for automotive exterior. Three polypropylene grades were used in this work: PP526P (MFI 8.0, ASTM 1238; density=0.90 g/cm³), supplied by Sabic, a homopolymer specially developed for cast film application; PP1105E1 (MFI 35, ASTM 1238; density=0.90g/cm³), supplied by ExxonMobil, a high melt flow rate homopolymer designed for general purpose injection molding; PP3485WZ (MFI 4.1, ASTM 1238; density=0.90g/cm³), supplied by TotalEnergies, a nucleated homopolymer designed for thermoforming. Three elastomer were used: a hydronated styrene-butadiene-styrene triblock copolymer, SEBS G1657 (MFI 22, ASTM

1238; density=0.90g/cm³), supplied from Kraton, which has a styrene to rubber ratio of 13/87 wt.% and consists of 65% triblock and 35% diblock.

2.2 Nanocomposites Preparation and Processing

2.2.1 Nanocomposite Preparation

Nanocomposites for the scopes of this work were prepared by melt intercalation which introduces high shear force during compaction of molten polymer for mixing with fillers. Prior to compounding, nanoclay was treated with silane treatment via a solvent-free process at Malvern Minerals Co. where the organoclay was exposed to a 0.8wt% refluxed silane vapor. This silane concentration was pre-determined as the optimized level for sufficient coupling. The treated organoclay was then sieved with a No. 200 mesh. A Leistritz twin screw extruder (diameter = 27 mm; L/D = 48) was used with processing temperature of 180 °C and RPM = 200. PP, PPgMA and treated nanoclay were fed from the hopper to the screw and are then pushed along the barrel chamber to be heated. A two-step compounding process involving a masterbatch and “let-down” was utilized. The masterbatch contained 1:1 clay: PPgMA concentration ratio and comparable loading of base PP. The “letdown” was then made by adding masterbatch to PP homopolymer to prepare nanocomposites with various clay loadings. It has been suggested that the melt flow properties of PP/silicate composites increased as quadratic function with increase of die diameter while it decreased with increased particle size [106]. A pelletizer BT 25 from Scheer Bay, Inc was used for granulation. Both compression molding and injection molding were used to prepare samples and test specimen.

2.2.2 Biaxial stretching

Development of the biaxial rig stretching instrument for pilot line and laboratory study has therefore driven huge interests as such enables the fundamental study of processing-

structure-property relationship in biaxially orientated polymer [107][108][109]. The laboratory evaluations also provide useful information on new formulation in shortened time which saves both time and effort. Biaxially orientation in this research was carried out on the Karo IV laboratory stretching machine at Brückner Maschinenbau GmbH & Co. KG, Siegsdorf, Germany. Stretch ratios up to 10 times in both the machine and transverse directions are possible with this device and the maximum stretching temperature could achieve 400 °C. Other advantage includes a potential second stretching oven for simulating the tenter production process. Specifically, in this work square specimen (90 mm × 90 mm) was cut from the melt-extruded PP and PPNC precursor sheets with ~1.2 mm thickness. The samples are heated using hot air to the desired temperature. After preheating, the samples were biaxially stretched under a range of processing conditions. During the biaxial stretching, the displacement and resulting forces at the clamps were recorded during the stretching process and stress-strain curves were generated based on these data.

2.2.3 Supercritical Batch Foaming

Basically, the physical supercritical batch foam process in this research involves four phases: 1) supersaturation of CO₂ into the sample at desired temperature; 2) cell nucleation due to the thermodynamic instability initialized by decrease in pressure, 3) cell growth due to an expansion caused by the release of CO₂; 4) cell stabilization via a cooling process induced by water bath. Specifically, disk samples of 2mm thickness prior to batch foaming were prepared via compression molding. Batch foaming occurs in non-stirred high-pressure vessel in stainless steel from Parr Instrument. A glass beaker was inserted to prevent contact between samples and vessel wall. A customized Teflon sheet was also inserted into the middle the beaker to help holding the sample in a free-standing fashion. Dry ice was the added as CO₂

source. The vessel was gradually heated to the preset temperature and pressure above supercritical point in a controlled manner. Once the temperature and pressure were achieved and then kept constant, the sample is immersed in supercritical CO₂ for predetermined time as 2 hours to obtain an equilibrium oversaturated state. Foaming was triggered via a rapid depressurization by releasing the gas valve. It should be mentioned that depressurization rate was very fast and could be approximately calculated as the average of pressure drop divided by depressurization time. The reaction vessel was transferred into cooling water bath immediately after gas releasing to stabilize the foam structure.

2.2.4 Injection molding and compression molding

A large number of products are produced by injection molding. In injection molding process, the compounded samples are preheated in cylindrical chamber to a temperature at which it can flow and then it is forced into a cold, closed mold cavity by means of quite high pressure, which is applied hydraulically through the ram or screw type plunger. The screw rotates to pick up the PE and melt it, mix the melt and deliver it to the closed mold. The screw is then moved forward to force a fixed volume of the molten polymer into the closed mold. After melting, PE is solidified in the cool mold, the screw rotates and moves backward to charge the polymer for the next cycle.

Compression molding is one of the comm polymer processing techniques, which contains stationary and movable molds. Polyethylene composite is placed between them and then the mold is closed, heat and pressure are applied to obtain a homogeneously shaped composite. Applied pressure and heat depend on the thermal and rheological properties of the polymer. A preheating time is needed to reduce holding time. Slow cooling or rapid cooling (quenching) can be applied at the end of holding time.

2.3 Characterization techniques

2.3.1 Rheology

Rheology is the study of how the deformation and flow of materials respond under applied stress. It is of particular importance for polymers, as their viscoelasticity can lead to a viscous or elastic behavior depending on the stress was applied. Rheology probes relationship of the property-structure of the polymer melts or polymer solutions. Understanding the rheological behavior is also essential to for polymer processing and optimization.

Shear rheology refers to the strain response when imposed to shear stress. Linear viscoelastic behavior describes the change of stress response under linear region (small strain) in oscillatory shear tests. A parallel plate geometry was used as the fixture where the material is positioned between a stationary bottom plate and a rotational top plate. A sinusoidal strain is applied to the polymer melt by top plate and the corresponding axial stress is measured by a pressure transducer connected to the top shaft. The oscillatory strain γ is and stress τ follow the relation:

$$\gamma(t) = \gamma_0 \sin(\omega t) \quad (2.1)$$

$$\tau(t) = \tau_0 \sin(\omega t + \delta) \quad (2.2)$$

Where ω is the frequency of the sinusoid, δ is the phase shift and usually called loss angle, γ_0 is the strain amplitude and τ_0 is the stress amplitude. The dynamic shear measurement is usually reported with storage modulus G' and loss modulus G'' as a function of frequency:

$$\tau(t) = \gamma_0 [G' \sin(\omega t) + G'' \cos(\omega t)] \quad (2.3)$$

Where G' and G'' represent solid-like property and liquid-like property, respectively. They are calculated from an amplitude ratio $G_d \equiv \tau_0/\gamma_0$ and δ as follows:

$$G' = G_d \cos(\delta) \quad (2.4)$$

$$G'' = G_d \sin(\delta) \quad (2.5)$$

Incorporating fillers to neat polymer changes its rheology. In this work, dynamic shear rheology of PP and PP clay nanocomposites was conducted on a TA Instruments AR2000 Rheometer with parallel plates of diameter of 25mm. Disk specimens were prepared by compression molding for both cast sheet samples and film samples after biaxial stretching in order to demonstrate the effect of biaxial orientation on the clay dispersion. The films samples were prepared via stacking multiple pieces of BOPP film in the compression molding. The test was carried out over a frequency range from 0.01 to 100 rad/s under a fixed strain of 1% in most cases. This was determined by oscillatory strain sweeps where the G' and η' were monitored as a function of strain at a fixed frequency to validate the viscoelastic regime.

Extensional rheology refers to the deformation response when exposed to extensional flow. The cross section of material is changing which differs from shear rheology where the cross section is fixed. Extensional rheology is critical in several polymer processing including foaming, blow molding, thermoforming and film blowing where an extension deformation is experienced. It probes the nonlinear behavior of the polymer in extensional deformation that cannot be illustrated by shear rheology. This is because the polymer chain is not fully stretched during shear tests. Extensional rheology measurement was conducted using an extensional viscosity fixture (EVF) fixture on a TA instruments ARES rheometer. The fixture consists of two drums: a fixed drum rotating around its axis, and a drum orbiting around the fixed drum while still rotating around its axis. During extensional test, the specimen is winded up by rotating drums and thus stretched rapidly by along one direction while width and thickness is decreased. Since the drum for force measuring is fixed and it can be coupled to the torque

transducer of the TA instruments ARES rheometer. The extensional stress ($\sigma_E(t)$) is determined by the extensional force at the sample derived from the measured torque as follows

$$\sigma_E(t) = \frac{F_s(t)}{A_s(t)} \quad (2.5)$$

where $F_s(t)$ is the extensional force and $A_s(t)$ is the cross section area perpendicular to stretching direction. The extensional strain rate is calculated based on the drum rotational rate as follows

$$\dot{\epsilon} = \frac{2\Omega R}{L_0} \quad (2.6)$$

where Ω is the angular rotation speed of the motor, R is the radius of drum and L_0 is the stretch zone gap length. Based on the extensional stress and extensional strain rate, the uniaxial extensional viscosity is calculated as follows

$$\eta_E(t) = \frac{\sigma_E(t)}{\dot{\epsilon}} \quad (2.7)$$

The extensional viscosity measurements were conducted at various strain rates over Hencky strains up to 3. In order to ensure that the specimen was uniformly stretched in the central portion during the test, the state of the stretched specimen was also inspected immediately after the test, so as to observe any sagging of the polymer melt due to gravity effect and any non-uniform stretching.

2.3.2 Thermal Analysis

The thermogravimetric analysis (TGA) is a technique in which the mass of a specimen is monitored by a precision balance, and the absolute amount and rate of weight loss is recorded as a function of temperature or time under controlled heating / cooling program in controlled atmosphere within a furnace. Therefore TGA analysis quantifies the components change in the sample as temperature increasing. In this work, TGA was used primarily to examine the thermal

stability of organoclay during the compounding process and post-processing process such as high temperature stretching. It can also be used to measure the organic content since the weight loss at high temperature is an indication of the volatile products from burnt organic components in either nanocomposite or organoclay. TGA analysis was conducted on a TA Instruments Q500 apparatus to evaluate the weight loss of various organoclays with increasing temperature. The About 10 mg of clay powder or nanocomposite was heated from room temperature to 800 °C using a high resolution ramp under a nitrogen atmosphere. The high resolution ramp varies the heating/cooling rate of the furnace in response to decomposition rate change of the sample to improve weight change resolution.

2.3.3 Transmission Electron Microscopy

Transmission electron microscopes (TEM) is a powerful microscope technique with base principles same as light optical microscope by using a particle beam of electrons as the illumination source to visualize specimen instead of light. According to Abbe's equation, the resolving power increases with decreasing wavelength of radiation. Because the wavelength of electrons is much smaller than light, it generates a typical resolution of as small as 0.2 nm, compared to 200nm in optical microscope. The beam transmitted through an ultra-thin specimen, which is usually less than 100nm, and the electrons either scatter or hit a fluorescent screen at the bottom of the microscope under high vacuum to produce images. An image of the specimen usually shown in different shades is formed directly by occlusion and absorption of electrons in the sample according to its density variation. The dark region on TEM image usually represents where the samples are thicker with large molecular weight or high atomic number that fewer electrons are transmitted through while the light region on TEM image are correlated to thin regions with small molecular weight of atoms that more electrons are

transmitted through. Particularly, TEM has been used in this dissertation to examine the dispersion state and orientation degree of organoclay nanoparticle in extruded PP-clay nanocomposite sheet and biaxially oriented PP-clay nanocomposite film. The dispersed clay layer appeared as the dark line while PP matrix appeared as lighted region. Due to the platy structure of layered silicate, the corresponding aspect ratio in each nanocomposite has been determined by measuring the length and thickness of the platelets presented in each TEM images via Image J software. The delamination state of nanoparticles was thus quantified.

In this study, the specimen for the TEM imaging was prepared using ultra-microtoming method by a PTXL ultra-microtome (RMC, Boeckeler Instruments) connected to a CRX cryo unit. A small rectangular piece was cut from extruded sheets and biaxially oriented films and 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. A JEOL100 CXII instrument was used to obtain TEM micrographs of these microtomed samples.

2.3.4 Scanning Electron Microscopy

Scanning Electron Microscope (SEM) is another type of electron microscope used for detecting topological information by using a focused beam of electrons to scan across of the surface specimens systematically. In a SEM system, a high vacuum is required. Electrons were generated and accelerated either from thermionic sources such as heated tungsten or lanthanum hexaboride gun, or field emission guns as more often used in modern SEM with a huge electric potential to draw electrons toward the anodes instead of heating filament [110]. The electron beam was then converged and collimated into a relatively parallel stream by an electromagnetic condenser lens and focused onto the specimen plane. to control electron beam. An electromagnetic deflection coils was used to control electron beam rastering across the

surface of a specimen. Unlike TEM which uses transmitted electrons, SEM employs emitted electrons. When a beam of electrons interacts with the sample, secondary electrons, backscattered electrons, and characteristic X-rays are produced while former two are commonly used for imaging samples. Secondary electrons (SE) have low energy and generates from inelastic scattering only from surface of the samples, therefore used principally for showing morphology on samples. Backscattered electrons (BSE) are a result of elastic scattering from a fairly large escape depth and therefore most valuable for showing topological information beneath the surface and also contrasts in composition in multiphase samples due to the dependence of the number of BSE on the atomic number. For imaging in tradition SEM, secondary electrons were detected by a detector, converted to a voltage and then amplified through an analogue signal processing on 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 projected on the surface, the detector collected a greater number of secondary electrons resulting a higher voltage and showing as a bright spot; In the contrast, when the beam is on a depression on the sample surface, the detector collected fewer number of secondary electrons leading to a smaller voltage and a dark spot on the surface of CRT. The SEM image is composed of systematically scanned spots with varied intensity on the CRT surface. For modern SEM, digital computer techniques have gradually replaced tradition CRTs.

For the work presented in this dissertation, scanning electronic micrographs (SEM) including both backscattered electron (BEI) and secondary electrons (SE) micrographs were obtained via JEOL 6610LV SEM. All samples used for SEM observation were cryogenically fractured after immersion in liquid nitrogen for 30 mins. The fractured cross-section surface was then sputter coated with gold. For biaxially oriented nanocomposite film, the MD-ND or TD-

ND plane of the specimen was observed to serve two purposes: 1, to verify the dispersion state of organoclay nanoparticle with presence or absence of agglomerates; 2, to examine film integrity regarding potential existence of cavities voids after stretching. For study in PP clay nanocomposite foam, the purpose of using SEM was to investigate the cell morphology and microstructure. Cell size distribution and mean diameter of cells were analyzed using Image J software by counting all the available cell shown in SEM micrographs. As for injection molded thermoplastic polyolefin (TPO) nanocomposites, the microstructure and morphology with an emphasis on dispersed rubber phase was examined. The darker regions represent the dispersed rubber phase while the lighter region represents the PP matrix in TPO.

2.3.5 X-ray Diffraction (XRD)

XRD has been used to characterize semicrystalline polymers regarding their crystal structures at the unit cell level [111]. The non-destructive technique was based on the fact when incident beam is scattered by periodic array with long range order, diffraction occurs, and constructive interference is produced at specific angles. In crystalline domains, atoms were arrayed in repeated units, and they act as diffraction sites when exposed to X-ray beam. When atoms were arranged in a different fashion, different diffraction exhibits indicating a different crystal structure. On the other hand, amorphous regions do not possess periodicity and therefore there was no diffraction pattern. For constructive interference, the wavelength of the X-ray beam and the incident angle of the X-ray beam follows Bragg's law.

$$n\lambda = 2d\sin\theta \quad (2.8)$$

where n is the order of reflection, λ is the wavelength of incident X-ray beam, d is the spacing between diffracting planes, and θ is the incident angle. Different diffraction patterns appear in 1D XRD profile as peaks with different position and intensity, which are essentially

determined by intensity of crystal structure. A Bragg-Brentano geometry was usually adopted where diffraction vector is always perpendicular to the sample surface.

XRD was utilized in this research to primarily to investigate the crystal structure of PP matrix in both extruded and biaxially oriented nanocomposite. A 1.3 mm slit was selected and mounted on the X-ray beam source side based on the resolution and intensity of the peak of interest. Sheets samples were mounted on a sample holder with plasticine and flattened with a glass plate. Film samples were mounted on top of sample plate specially designed for thin films which has an X-ray transparent flat surface. For polymer sheets and films less than 2 mm, X-ray can penetrate thoroughly, and thus bulk microstructure can be revealed. In addition, the d-spacing of inter planes of the organoclay was also investigated as secondary tool to validate its dispersion state in nanocomposite. The d-spacing for montmorillonite (001) basal plane is 0.95 nm. Intercalation between galleries of clay resulted in an expansion of d-spacing which appears as a left shift of corresponding peaks. However, while the d-spacing of the clay layers in the nanocomposite were more relied on TEM and rheology. Morgan and Gilman [112] conducted a comparative study characterization of polymer/clay nanocomposites by TEM and XRD and they suggested that XRD alone may be inadequate to character the dispersion of clay platelets in polymer matrix while TEM need to be combined.

2.3.6 Small Angle X-ray scattering

Small-angle X-ray scattering (SAXS) is another X-ray scattering techniques for structure characterization by detecting the scattered intensity of an X-ray beam when interacting with a sample as function of incident and scattered angle. As the name suggested, the incident angle is very small (0.1° to 5°). According to Bragg's Law, the length scale of subject is inversely proportional to the scattering angle and therefore SAXS can be used to

revolve structural information of subjects with length scale from nanometers to micrometers. The scattered intensity is a product of form factor and structure factor. A scattering vector q is usually used in SAXS to describe the deflected beam instead of scattering angle 2θ as follows:

$$q = \frac{4\pi \sin \theta}{\lambda} \quad (2.9)$$

For semicrystalline polymers, SAXS has been used to study the long-range order of periodic crystalline structure especially lamellar structures arranged in a stack form a diffraction grating. In this work, the crystalline morphology in PP nanocomposite at different processing states was investigated via 2D SAXS pattern which was obtained at Beamline 12-ID-B Advanced Photon Source of Argonne National Laboratory with a x-ray energy of 13.3 keV ($\lambda = 0.9347 \text{ \AA}$). The scattered x-ray intensities were measured using a two-dimensional (2-D) Pilatus 2M detector. The sample to detector distance was set to 2.0 m and for film samples, the detecting range of scattering vector ranges from 0.0035 to $0.9 \text{ \AA}^{-1}$. The scattering signal from air is collected as well and subtracted from the sample signal. Moreover, through 1D integrated intensity curves, the peak position of scattering vector q can be obtained, which correlates to the period structure such as long period of lamellae. In addition, inter-layer information of clay powder were also studied by SAXS.

2.3.7 Permeability Measurement

The barrier performance for packaging films is usually quantified by the permeability to gases. Permeability describes the ease with which a permeant molecule can flow through a solid driven by the permeant concentration difference and is defined as the mass of diffusing species per unit time per unit area according to Fick's Law of diffusion. In a typical permeability measurement, a barrier film is inserted in the middle of a tunnel which is thus separated into two cells. The testing gas is fed on one side of the cell and gas permeated through

the film to the other side of cell is carried away by a sweep gas. In practical, transmission rate is considered as the most common way to describe flux of gas diffusing through a polymer.

In this work, permeability of biaxially oriented films was measured with Mocon Ox-Tran 2/21 unit was used for oxygen, and a Mocon Permatran-W 3/33 unit was used for water vapor according to ASTM D3985. Both instruments were calibrated at 23°C with a standard film of known permeability provided by Mocon. The test specimens cut from middle portion of films were mounted and laminated with a 5cm² size aluminum mask. to reduce the exposed area. Oxygen permeability were conducted at 23 °C and 0% RH while water vapor were conducted at 25 °C and 100% RH. All results are calibrated to a film of 1 mil thickness.

2.3.8 Optical Property Measurement

Total transmittance and haze can be used to describe the optical appearance of a transparent object. Total transmittance refers to the ratio of transmitted light to the incident light while haze describes the degree of blurry in a transparent material as defined by the ratio of scatter light to the incident light. In this dissertation, the optical performance of biaxially oriented nanocomposite films was characterized by a UV-Vis spectrometer with wavelength range from 400nm to 800nm. Optical measurement of TPO nanocomposite was conducted on a Rhopoint ID-TX imaging transmission appearance meter which utilizes an imaging-based analysis [113]. The Rhopoint ID-TX Transmission Haze meter quantifies the transmission appearance of uncolored transparent, semi-transparent and translucent samples such as plastic, films, glass and liquids. The instrument uses a high specification camera to take images of a specially designed target graticule through the sample to be analyzed. The samples were placed atop the graticule, either in direct contact or at a predetermined spacer. Transmittance and haze value were obtained after image acquisition and data processing using the instrument's built-

in software.

2.3.9 Mechanical Property Measurement

Tensile test was measured with an Instron 5565 universal testing machine using film fixture according to ASTM D638. The mechanical behavior under static axial tension was determined. A thin slice of 2.54 cm wide and 10 cm long was cut from the middle portion of the biaxial stretched films. Specimens from MD and TD were stretched uniaxially at ambient temperature and a strain rate was 50mm/min until fracture. 1% secant modulus was calculated.

The quasi-static compression test of PP and PP clay nanocomposite foams was characterized in uniaxial compression carried out on a universal testing machine, Instron 5982, at room temperature under quasi-static conditions, employing a displacement rate of 0.01 s⁻¹ depending on the sample geometry. The quasi-static compression was conducted by using a hydraulic driven system with a load cell of 100 KN. The foams were compressed to a maximum strain of 90%. The compression force load and crosshead displacement were measured and recorded by the Instron machine.

Flexural test was conducted with a United Testing Systems (UTS) model SFM-20 according to ASTM-D790. A three-point bending configuration was applied, and flexural modulus was obtained as the ratio of stress to strain in a flexural deformation of a material.

Notched Izod impact test was conducted with an TMI impact testing machine at ambient temperature according to ASTM-D256 The test employs a with a standardized pendulum-type hammer and breaks the test specimen with on pendulum swing to determine the resistance to break. Samples were notched and conditioned at least 24 hrs before testing, which produces a stress concentration that increases the probability of a brittle failure. The results were reported as energy absorbed per unit cross-sectional area.

Chapter 3. High-Barrier Film from Biaxially Oriented Polypropylene Clay Nanocomposites: Structure and Properties

3.1 Introduction

Biaxially oriented polypropylene (BOPP) films have driven extensive interests in recent decades with broad application including food packaging, labelling, cable insulation, shrinkable warps and capacitor films [114]. This is due to their advantage such as low density, cost reduction, good mechanical, high clarity, temperature service window, moisture resistance, no-toxicity, printability, dielectric breakdown strength and stability with environmental changes [3,5–7]. Particularly, BOPP represents one of the largest component in transparent flexible packaging film market which requires adequate barrier, optical transparency, and mechanical robustness.

Improving the oxygen barrier performance in polymer packaging films has always been demanding to support the growing need for 1) preserving better-quality foods or non-food products with extended shelf life and 2) reducing the usage of material such as aluminum foil while maintaining same performance to help with sustainability. To achieve this goal, various efforts have been developed to further improve barrier property of biaxially oriented films such as multilayer coextrusion, blending, surface coating and metallization [4,50–55]. However, these methods are associated with increased instrumental complexity, volatile organic solvents, and high energy consumption. Alternatively, incorporating nanofillers with high aspect ratio into the polymer matrix has been a facile method in improving nanocomposites property including the barrier [57,61]. These impermeable fillers impede the diffusion of gas molecules by forcing them in a more tortuous pathway. Nanoclay, also known as layered silicate, has gained great attention due to its high modulus, impermeability, low cost, heat

resistance, flame retardancy, availability and ease to melt mix with polymers [57]. Their layered structure allows them to be delaminated into thinner layers or even exfoliated into single platelets and their chemical nature allows them to be modified with organic ions. Compared with conventional filled composites, high aspect ratio of these layered silicates give rise to more polymer-filler interface sites which accounts for drastic reinforcement not only in barrier but also modulus and flammability. It has been well established that the state of nanoclay delamination and orientation plays a vital role in determining the nanocomposite macroscopic property. Organic modification of hydrophilic clay via ion exchange and a maleic anhydride-grafted PP compatibilizer has been commonly adopted to promote clay dispersion in such systems [82].

However, there is conflict in application of nanoclay when it comes to biaxial orientation. On one hand, in a typical BOPP manufacturing, the preform is subjected to a typical deformation ratio such as 6×6 in simultaneous biaxial orientation process [3]. The high area stretching ratio is critical as such endows the base polymer with enhanced mechanical and barrier. Consequently, high stress and narrow temperature sensitivity are also encountered during this rapid biaxial deformation especially for BOPP which is known to draw highest stress over other comm polymers [16]. On the other hand, presence of rigid nanoparticles may have a detrimental effect on stretchability due to their inherent incompatibility, heterogeneity, and local stress concentration effect. Under high stress, debonding between filler and matrix may occur which result in undesirable cavitation or early breakage occurs with limited stretching ratio and even reversed effect of decrease in barrier in the final film [97,98]. In addition, the presence of cavitation or aggregates will act as light scatter which lead to dramatic loss in transparency, which is undesirable in transparent

packaging. Such detrimental effect could be more significant with increasing concentration of clay nanoparticles as the potential to form aggregates is higher [99,100]. As a result, there has been scarce work related to biaxially orientated polymer clay nanocomposite film especially polypropylene-clay nanocomposite film. Either a limited area stretching ratio was reported which fell short of commercial production line [39,103], or the composite was prepared as a coating layer instead of into the matrix or core layer [101]. Moreover, a portion of available work on biaxially oriented polymer nanocomposite actually serves the purpose to introduce cavitation for porous film [102,115].

To obtain stretchability and reinforcement without sacrificing other properties, achieving sufficient interfacial adhesion to overcome the debonding stress between polar layered silicate and the non-polar polymer matrix is crucial. More recently, our group has reported a strategy to achieve enhanced interfacial interaction via a masterbatch method incorporating solvent-free vapor phase silane-treated organoclay coupled to high-molecular weight functionalized PPgMA compatibilizer [74,75,89]. The vapor phase treatment provides enhanced silane penetration into the interlayer galleries. The reactive coupling occurring at both faces and edges of silicate layers allows significantly enhanced interfacial adhesion and improved nanoparticle dispersion. Improved rheological behavior in the form of greater melt straining hardening during extension flow promotes nanocomposite processability in foaming and blown film application, which shed further light in the potential for biaxially stretched film process.

In this paper, PP/clay nanocomposite prepared from masterbatch additives incorporating silylated organoclay and a maleated propylene compatibilizer was biaxially stretched at conditions close to industrial manufacturing. The aim is to produce transparent

biaxially orientate nanocomposite film with improved barrier. It is anticipated that nanoclay in our masterbatch will stay well dispersed during biaxial stretching thus allowing high stretchability and transparency in final film. Matrix crystalline structure will also be affected. Therefore the effect of nanoclay as well as biaxial stretching on the resulting structure and properties of biaxially oriented nanocomposite films is yet to be explored. To the author's best knowledge, an area stretching ratio of 7×7 was reported for the first time in biaxially stretched PP/clay nanocomposite film with up to 10wt% clay loading. Although there have been extensive efforts to understand the structure and property of pure BOPP films [26,31,32,116], the knowledge of such in biaxial oriented polypropylene clay nanocomposite is lacking. It is therefore of great interest to understand how the presence of organoclay influences the biaxial orientation process and consequently microstructure-property in the nanocomposite film. The effect of high-strain biaxial stretching and addition of organoclay on the microstructure and property in final film was demonstrated.

3.2 Materials and Characterization

3.2.1 Materials

The polypropylene grade used in this work was PP526P supplied by Sabic, (MFI 8.0, ASTM 1238; density=0.90 g/cm³). The maleic anhydride-grafted PP (PPgMA) compatibilizer grade was Exxelor PO-1015 supplied by ExxonMobil, which is a random copolymer with ethylene ($M_w = 123,000$; 0.42wt% bound maleic anhydride). Organically modified montmorillonite Nanomer I.44P was obtained from Nanocor, which has a quaternary ammonium ion surfactant with two octadecyl tails. The reactive silane coupling agent was Dynasylan 1411, an aminoalkyl dimethoxysilane from Evonik.

3.2.2 Nanocomposite Processing

The silane treatment was conducted via a solvent-free process at Malvern Minerals Co. where the organoclay was exposed to a 0.8wt% refluxed silane vapor. This silane concentration was pre-determined as the optimized level for sufficient coupling. The treated organoclay was then sieved with a No. 200 mesh. Nanocomposites incorporating PP, PPgMA, and treated organoclay were compounded in a Leistritz twin screw extruder (diameter = 27 mm; L/D = 48) at 180 °C and RPM = 200. Before compounding, the PPgMA and grafted organoclay were dried in vacuum oven to remove moisture. A two-step compounding process involving a masterbatch and “let-down” was utilized. The masterbatch contained 1:1 clay: PPgMA concentration ratio and comparable loading of base PP to improve the mixing. The “letdown” was then made by adding masterbatch to PP homopolymer to prepare nanocomposites with various clay loadings. The final composition of nanocomposites was presented in Table 1. Sheets with thickness of approximately 1.2 mm for biaxial orientation were prepared in a single screw sheet extrusion line.

Table 3.1 Compositions of PP/clay nanocomposites.

	Polymer matrix	Amount of clay (wt%)	PPgMA to clay ratio
PPNC2	PP(MFI 8.0)	2	1:1
PPNC5	PP(MFI 8.0)	5	1:1
PPNC10	PP(MFI 8.0)	10	1:1

3.2.3 Biaxial Orientation

Square specimen (90 mm × 90 mm) was cut from the melt-extruded PP and PPNC precursor sheets with ~1.2 mm thickness and prepared for stretching. Simultaneous equal-

biaxial stretching was carried out with a Karo IV apparatus at Bruckner, Siegsdorf, Germany. The annealing oven as well as the stretching oven were held at 156 °C for partly molten state and a strain rate of 200% s⁻¹ was selected. Forces and displacements were recorded simultaneously during the stretching process and stress-strain curves were generated based on these data. A trial run was carried out to probe the stretching limit, then a following run was carried out to stretch samples to an area stretching ratio of 7 × 7 if possible, based on first trial run. Final films were achieved with ~25microns thickness and labelled as BOPP, BOPPNC2, BOPPNC5, BOPPNC10, respectively. In this paper, PP and PPNC will refer to the extruded sheets before biaxial stretching while BOPP and BOPPNC represent stretched films after biaxial orientation.

3.2.4 Characterization

The uniformity and transparency of biaxially stretched films were initially judged by eye. A PerkinElmer Lambda-800 Ultraviolet-visible spectrometer was used for light transmission measurement from visible light range (400 nm to 700 nm) to quantify the clarity of biaxially oriented film. The thickness of the film was measured with a micrometer along MD from center to the edge of the film at a fixed interval. Repeated measurements were conducted not only to obtain more reliable results but also to check the film uniformity.

A JEOL 100CXII transmission electron microscope has been used to investigate and assess the structure of composite. The images were obtained operated at a voltage of 80kv. A 90nm-thin slice of biaxially oriented film was prepared by microtoming perpendicular to the film direction and collected onto a 300-mesh copper grid. TEM images were used to assess the dispersion and orientation of clay particles or nanolayers.

Dynamic shear viscosity test was performed using TA ARES rheometer with 25 mm

parallel plates. A frequency sweep was conducted over a range of 0.01 rads/s to 100 rads/s at 200 °C under nitrogen. A fixed strain of 1% was applied within linear viscoelastic range as pre-determined. Disk specimens were prepared by compression molding for both cast sheet samples and film samples after biaxial stretching in order to demonstrate the effect of biaxial orientation on the clay dispersion. The films samples were prepared via stacking multiple pieces of BOPP film in the compression molding.

The Wide-angle X-ray Diffraction (WAXD) measurements to investigate the crystal structure of PP and PP nanocomposites were conducted using a Bruker D8 advance diffractometer. The source X-ray wavelength was 0.154 nm from monochromatic $\text{CuK}\alpha$ radiation. The diffractometer was set at a voltage of 40 kV, current of 40 mA and a 1.3 mm slit. Sheets samples were mounted on a sample holder with plasticine and flattened with a glass plate. Film samples were mounted on top of sample plate specially designed for thin films which has an X-ray transparent flat surface. For polymer sheets and films less than 2 mm, X-ray can penetrate through effectively and thus bulk microstructure being revealed. The 2θ scan angles were set from 8° to 30° , with a step size of 0.015 and a dwell time of 0.5 second. The degree of crystallinity was estimated by computing the area under the peaks of the XRD patterns. To be clear, lamellae in this paper refers to fundamental building block for either stacked lamellae or fibril. The degree of relative crystallinity estimated from the WAXD patterns has been estimated according to Hermans and Weidinger [117] with total crystalline and amorphous areas of the diffractogram.

Small-angle X-ray Scattering (SAXS) was performed at Beamline 12-ID-B Advanced Photon Source of Argonne National Laboratory with the x-ray energy of 13.3 keV ($\lambda = 0.9347$ Å). The scattered x-ray intensities were measured using a two-dimensional (2-D) Pilatus 2M

detector. The sample to detector distance was set to 2.0 m and the detecting range of the scattering wave vector $Q = 4\pi\sin\theta/\lambda$ ranges from 0.0035 to 0.9 Å⁻¹, where 2θ is the scattering angle. The long period of the lamellae correlates to scattering vector of the corresponding peak. All SAXS results were corrected for background scattering. An intensity screening was also conducted for sufficient intensity level.

The mechanical properties of oriented films were measured with an Instron 5565 universal testing machine using film fixture according to ASTM D638. A thin slice of 2.54 cm wide and 10cm long was cut from the middle portion of the biaxial stretched films with a specialized cutting stage to eliminate the rough edges which could lead to early fracture. Specimens from MD and TD were stretched uniaxially at ambient temperature and a strain rate was 50mm/min until fracture. 1% secant modulus was calculated. Measurements on five different specimens were averaged.

A Mocon Ox-Tran 2/21 unit was used for OTR measurements, and a Mocon Permatran-W 3/33 unit was used for WVTR measurements according to ASTM D3985. Both instruments were calibrated at 23°C with a standard film of known permeability provided by Mocon. The test specimens cut from middle portion of films were mounted and laminated with a 5cm² size aluminum mask provided from Mocon Inc. to reduce the exposed area. OTR measurements were conducted at 23 °C and 0% RH while WVTR measurements were conducted at 25 °C and 100% RH. Two specimens from the same film were tested to obtain the average permeability. All results are calibrated to a film of 1 mil thickness.

3.3 Results and Discussion

3.3.1 Biaxial stretching behavior

This research is only focused on equal-simultaneous biaxial stretching. Figure 3.1

Representative stress-strain curve of PP and PPNC during simultaneous biaxial stretching at 156 °C (equally along MD and TD at 200% s⁻¹) shows the nominal stress-strain curves in MD and TD for neat PP and PP/clay nanocomposite (PPNC5 as representative) during simultaneous biaxial stretching at 156 °C and strain rate of 200% s⁻¹. For either along MD or TD, the stress-strain curves in this semi-solid process followed a typical ductile deformation behavior in tensile of semi-crystalline polymer with yielding, softening plateau and strain hardening. Such profile suggested the original crystal structure in the extruded sheet was destroyed and transformed into fibrils along the two stretching directions. Tensile modulus and yielding stress were found to be higher for the nanocomposites. This could be correlated with addition of rigid fillers and the increased remaining crystallinity from initial extruded composite sheet. PP and PPNC showed similar trend of strain hardening at later stage of biaxial stretching. For both PP and PPNC, the stress level along TD at early stage of stretching was higher than that along MD.

Clearly, Figure 3.1 shows that an area stretching ratio of 7*7 without breakage or cavitation were achieved for both neat PP and PP/clay nanocomposite film. Such deformation ratio is a critical criterion for obtaining thin films during a commercial semi-solid BOPP process. Incorporating rigid fillers in polymer matrix usually could result in a detrimental effect in film stretch-ability. The high stretch ratio also indicates the effectiveness of enhanced interface coupling between nanolayers and polymer matrix.

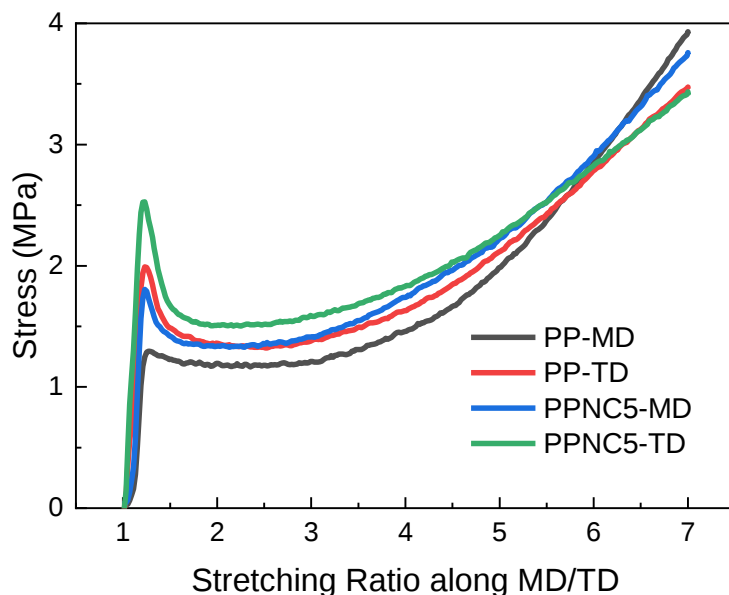


Figure 3.1 Representative stress-strain curve of PP and PPNC during simultaneous biaxial stretching at 156 °C (equally along MD and TD at 200% s⁻¹).

3.3.2 Stretched film appearance

All biaxially oriented BOPP and BOPPNPC films of 25-micron thickness exhibited high clarity without any voids. This was confirmed by visual inspection under an optical microscope as well as scanning electron microscopy. Representative photos of BOPPNPC5 film under room light condition were shown in Figure 3.2 (a). The transmittance measurements from a UV-Vis spectrometer have been presented in Figure 3.2 (b). Both neat BOPP film and BOPPNPC film show high transmittance in the visible light range, i.e., from 400nm to 700 nm wavelength. The presence of nanolayers with lengths of 250 nm at loadings up to 10 wt% clay did not degrade light transmission significantly as expected because scattering would be minimal from particles that are smaller than the wavelength of light.

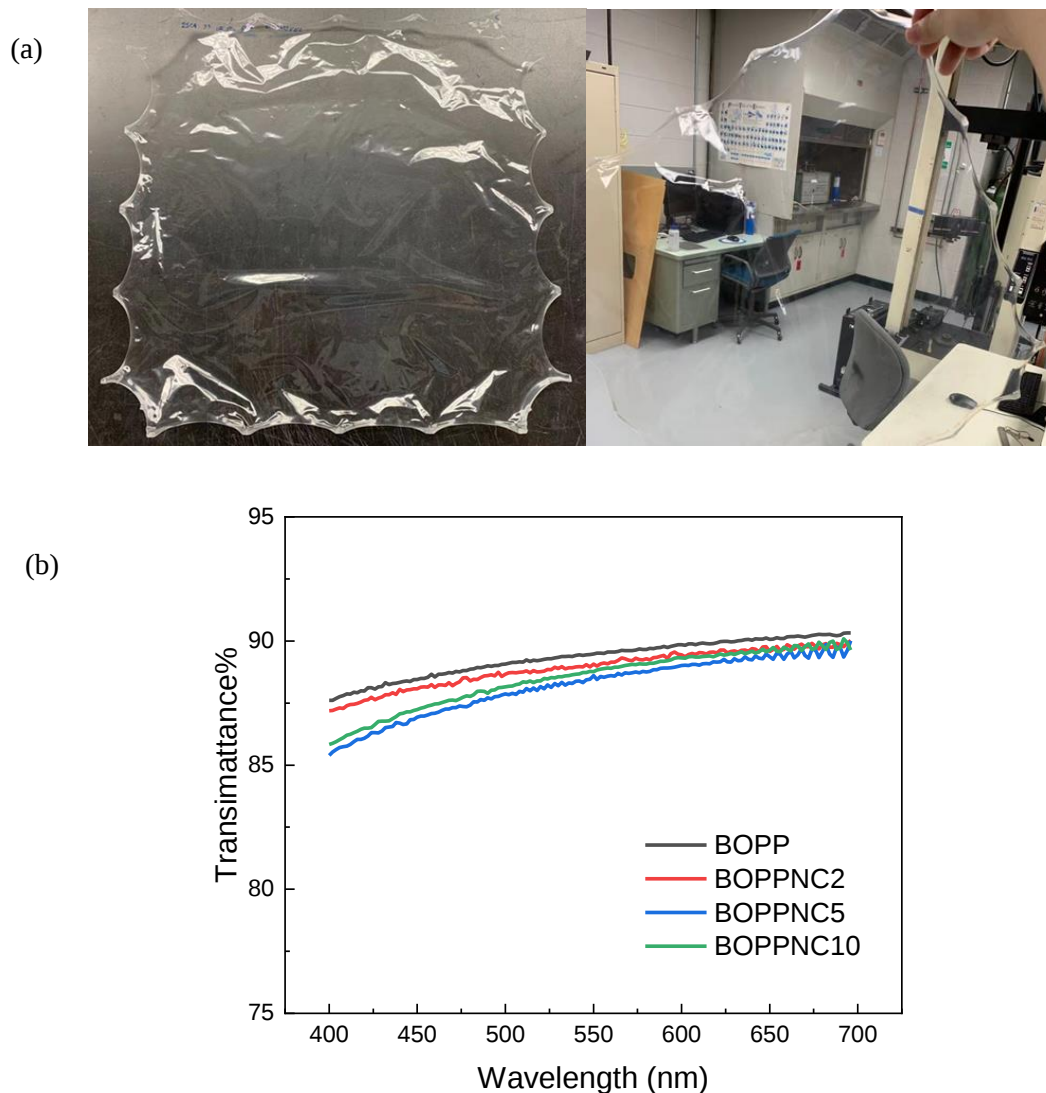


Figure 3.2 Optical performance of 25-micron thick BOPP and BOPPNC films, (a)top: optical appearance of representative BOPPNC5 film; (b) bottom: transmittance of 25-micron thick BOPP and BOPPNC films.

The thickness profile of BOPP and BOPPNC measured by micrometer exhibits high uniformity within a radiance of 33cm from the center of the film as shown in Figure 3.3 (a)(b)(c)(d). Only the edges becoming thicker due to the location of clamping. The attainment of transparency and uniform thickness without any cavitation across the main film granted its capacity in high transparent packaging.

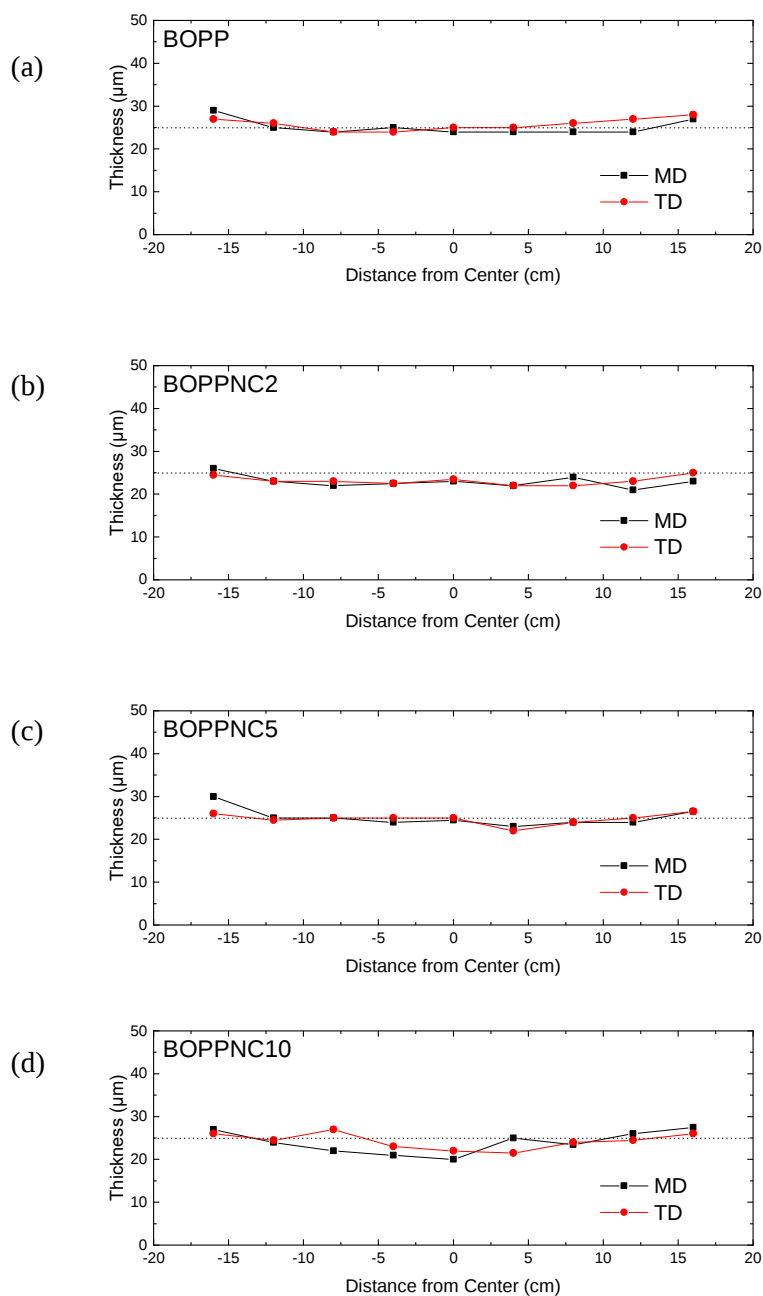


Figure 3.3 Thickness profile along MD and TD in various films.

3.3.3 Nanoclay dispersion

The state of nanoclay delamination and orientation plays a vital role in determining the nanocomposite macroscopic property. It has been well established the dispersion of clay particles range from agglomeration, intercalation to exfoliation in polymer-layered silicate

composites. The morphology of the biaxially stretched nanocomposite films was observed with transmission electron micrographs as shown in Figure 3.4 with BOPPC5 as a representative. Figure 3.4 (a) represents clay dispersion in extruded sheets where clay particles have been partially delaminated with few tactoids remaining and oriented in plane as a result of high shear during compounding and initial stretching during sheet extrusion. Figure 3.4 (b) corresponds to nanocomposite film after biaxial stretching. The arrow in the image indicated film thickness direction. It is evident more clay nanolayers were oriented in plane and more nanolayer exfoliation occurs after biaxial stretching. This also correlates to the fact that the diffraction peak for clay (001) plane revealed by WAXD was almost diminished after biaxial stretching. Improved clay platelets dispersion after biaxial stretching was also reported in various biaxially oriented polymer/clay nanocomposites [103,104,118]. Clay nanolayers orientation and exfoliation were raised to higher extent after such a high stretching ratio.

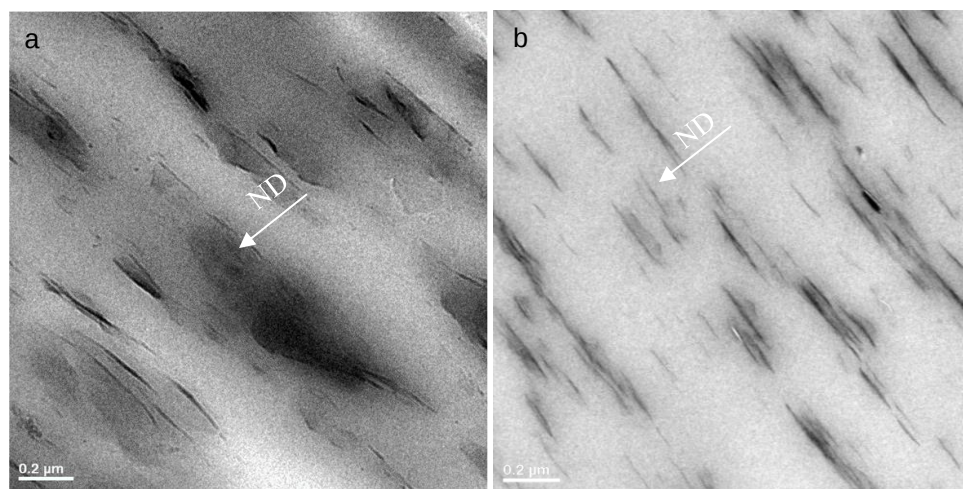


Figure 3.4 TEM of PPNC5 (a) before stretching and (b) BOPPC5 after stretching, scale bar 0.2μm.

While TEM provides direct information, it only probes a relatively small volume. Dynamic shear rheology was evaluated to be representative of composite nanostructure and

dispersion on a macroscale. The increase of dynamic viscosity and storage modulus at low frequencies indicated a good dispersion state of nanolayers [119,120]. As shown in Figure 5, the nanocomposites displayed increased dynamic viscosity and storage modulus at low frequencies compared to neat PP at same processing stage, i.e. PPNC5 compared to PP, BOPPPNC5 compared to BOPP. This may be related to the hindered polymer chains via increased entanglements between polymer matrix and dispersed clay nanoplatelets.

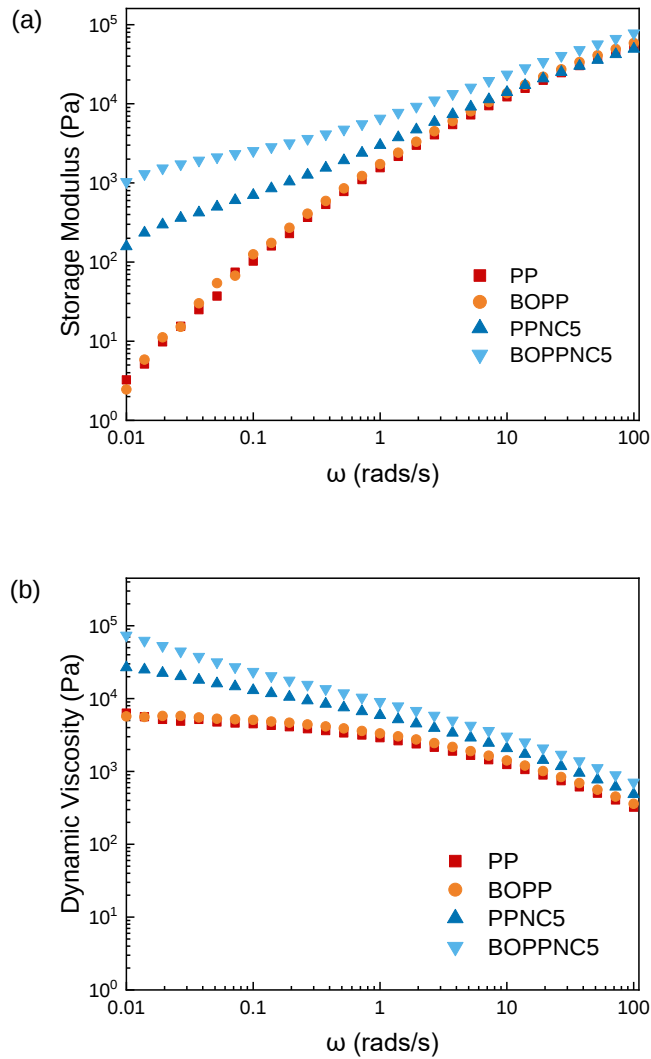


Figure 3.5 Dynamic Shear Rheology of PPNC before stretching and BOPPPNC after stretching (a) storage modulus (b) dynamic viscosity.

On the other hand, neat PP and BOPP showed similar rheology profile indicating biaxial orientation process did not cause significant macromolecule breakage. In contrast, the nanocomposites with the same clay ratio showed further increase in storage modulus and dynamic viscosity after biaxial stretching, e.g. BOPPN5 compared to PPNC5. This is a sign of increased interfacial interaction rise from improved dispersion.

A quantitative correlation between nanofiller concentration, aspect ratio, and the increment in dynamic viscosity was suggested [121–123] based on Maron-Pierce equation.

$$\frac{\eta'}{\eta'_m} = \left(1 - \frac{\phi}{\phi_m}\right)^{-2} \quad (3.1)$$

Where η' is the dynamic viscosity of nanocomposite, η'_m is the dynamic viscosity of neat PP matrix, ϕ is the volume fraction of nanoclay and ϕ_m is the maximum packing volume fraction. ϕ_m is correlated to the aspect ratio, a , of nanolayers as follows [121,122]:

$$\phi_m = \frac{3.55}{a} \quad (3.2)$$

The maximum packing volume fraction was first estimated based on the increment of dynamic viscosity data and then the effective aspect ratio was determined. The calculations were summarized in Table 2 and provide reasonable estimation. For example, the calculated aspect ratio of nanolayers in BOPPN5 was 64.0 which is close to 60.5 measured from TEM. Table 2 revealed that the clay aspect ratio in nanocomposite increased after biaxial stretching indicating a further extent of delamination and exfoliation which is in accordance with TEM observed results. It is worth mentioning that BOPPN5 presented the highest dispersion level which may be a result of optimal state between increased processing viscosity and total amount of clay particles.

Table 3.2 Effective aspect ratio of clay nanolayers.

	Extruded Sheets			Biaxially Oriented Films		
	PPNC2	PPNC5	PPNC10	BOPPNC2	BOPPNC5	BOPPNC10
Aspect ratio	47.1	52.3	36.8	55.7	64.0	40.3

3.3.4 Crystal structure

To further understand the nanocomposite structure, not only the dispersed clay nanolayer was investigated, but also the PP matrix crystalline microstructure need to be analyzed. Both WAXD and SAXS have been used to characterize the crystalline phase. The 1D X-ray diffraction patterns of extruded sheets and biaxial oriented films are displayed in Figure 3.6 WAXD patterns of PP and nanocomposites (a)Extruded (b)Biaxial stretched. The profile of each sample has been shifted for better comparison. Diffraction peaks at $2\theta = 13.8^\circ$, 16.7° , 18.3° , 21.2° and 25.0° corresponding to reflection lattice planes (110), (040), (130), (111), (060) revealed the presence of well-established α -form monoclinic crystal structure in isotactic PP [124]. A perseverance of α -form was confirmed and this indicated that the clay particles were dispersed at nanoscale, unlike micron-sized particles which could act as a versatile nucleating agent to introduce β -form crystal [125].

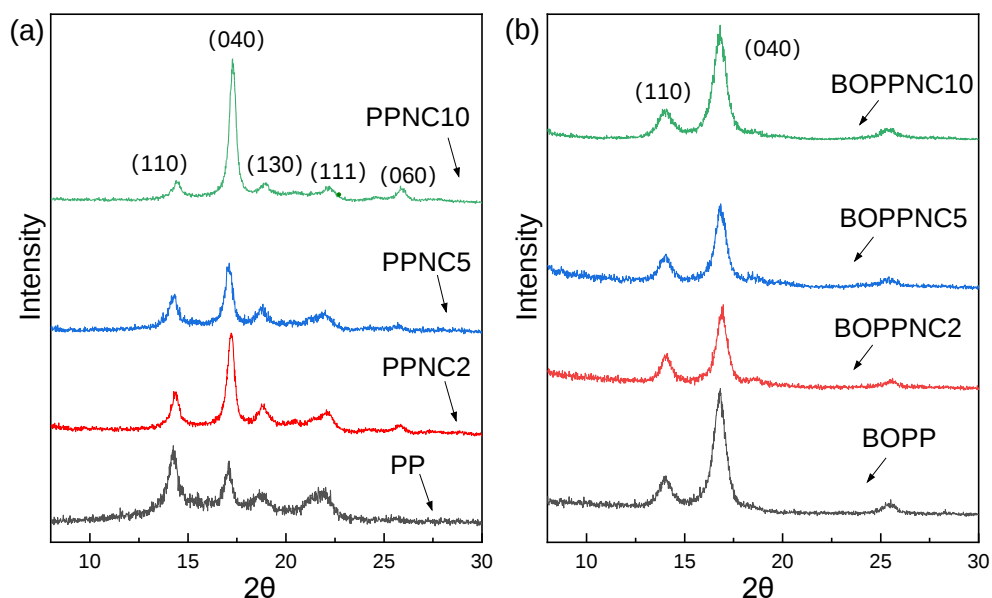


Figure 3.6 WAXD patterns of PP and nanocomposites (a)Extruded (b)Biaxial stretched.

With a monochromatic incident beam, the diffraction peak in 1D WAXD is a sequence of crystallite or lamellae with specific orientation where the Bragg condition is met. Since in the setup the incident beam is projected perpendicular to the film plane, each peak represents these crystallites oriented in such direction where the corresponding lattice plane parallel to the film plane. The higher the peak intensity, the larger the fraction of oriented crystallite. With this regard, a qualitative comparison could be conducted at same film thickness. In extruded PP sheet, all four characteristic peaks were present, which come from the remaining spherulite or randomly distributed or oriented lamella via the extrusion process. Addition of nanoclay give rise to a much more pervasive (040) peak. Platelet particles align parallel to the film plane during processing and provide nucleation sites with (040) planes of PP crystal piling on the plate plane of fillers, thus inducing a stronger b-axis orientation to film thickness direction [126]. A similar result was also reported by Kim et al. [77] where they found an intensity increase in (040) over (110) in hybrids with well-dispersed exfoliated silicate but not in agglomerated ones. It is speculated that the surface of these well-dispersed silicate induces

the crystal growth in (040) direction.

There was no change of peak position but with diminishing intensities of several peak induced by biaxial stretching process indicating that α -PP conformation did not change. Such α -form crystals perfection maintained at high drawing temperature has been reported [127]. After biaxial stretching, the intensity of (111) and (130) reflections were almost diminished in BOPP. This is a sign of highly oriented lamellar structure as suggested by Samios et al [128]. The dominating (040) peak represent the large fraction of in-plane oriented induced by biaxial stretching. BOPPNC showed similar trend with a slightly increased (040) peak intensity with increasing clay content indicating an amplified in-plane crystal orientation. This may also explain the more balanced elongation to break in MD and TD in BOPPNC.

Apparent crystallinity obtained from WAXD are summarized in Table 3. It is evident crystallinity increased in both PP and nanocomposite after biaxial stretching as expected due to strain-induced crystallization where disentangled amorphous polymer chains or smaller crystal fragments from initial lamellae could rearrange and recrystallize. Addition of nanoclay cause a slightly increase in crystallinity in extruded sheets. Nevertheless, there is no distinctive difference in the final crystallinity achieved in BOPP and BOPPNC film, probably because strain-induced crystallization dominates under such high strains.

Table 3.3 Estimated Crystallinity and crystallite size (D_{040}) of PP and nanocomposite before and after stretching.

	Extruded Sheets				Biaxially Oriented Films			
	PP	PP NC2	PP NC5	PPN C10	BOPP	BOPP NC2	BOPP NC5	BOPP NC10
Apparent Crystallinity	51.7%	55.6%	54.9%	56.8%	82.7%	81.9%	81.6%	80.9%

A 2D-SAXS pattern of neat PP and PP nanocomposites before and after biaxial stretching is shown in Figure 3.7. 2D SAXS pattern of PP and nanocomposites before and after stretching, where the meridian and equatorial represent MD and TD respectively. Before stretching, two maxima are shown along the meridian indicating the lightly oriented lamellar stacks in MD. This is due to the slight stretching during the sheet extrusion process. There coexists these unoriented lamellar or spherulites. After biaxial stretching, a ring pattern presents in both unfilled and filled films. This is a sign of the isotropous in-plane oriented lamellae. After a high ratio stretching, the original oriented crystals and remaining spherulites are fragmented into smaller lamellae. These lamellae are oriented but also randomly distributed along the film plane forming a fibrous network. In addition, the ring pattern of BOPPNC were more uniform compared with BOPP indicating an increased crystalline isotropy with more uniformly in-plane distributed lamella in BOPPNC.

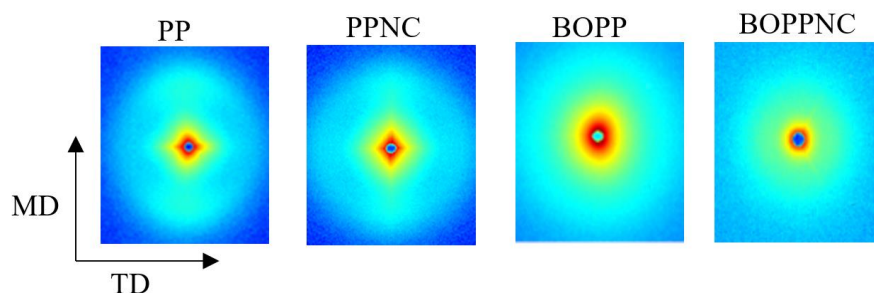


Figure 3.7 2D SAXS pattern of PP and nanocomposites before and after stretching.

1D integrated SAXS intensity profile for PP and PPNC before and after biaxial stretching was acquired and shown in Figure 3.8. 1D SAXS intensity profile of PP, nanocomposites and clay (a) Extruded (b) Biaxial stretched where x-axis represents the scattering vector q and y-axis is the Lorentz corrected intensity. Through 1D integrated intensity curves, the peak position of q can be correlated to the periodic structure. As shown in Figure 3.8 (a) (b), a peak

can be observed in the low q range ($<0.5 \text{ nm}^{-1}$) in every sample which was attributed to the long period of in-plane oriented lamellar stacks. Additionally, 1D SAXS intensity curves of clay I.44P as received and silane treated clay I.44P were obtained. A first order peak was observed around 2 nm^{-1} in both samples corresponding to their gallery structure. With silane treatment, the peak shifted left slightly indicating the further expansion of galleries. Moreover, while comparison of SAXS intensity profile between PPNC and clay proves that smaller q peak less than 0.5 nm^{-1} in PPNC represents signal from lamellae.

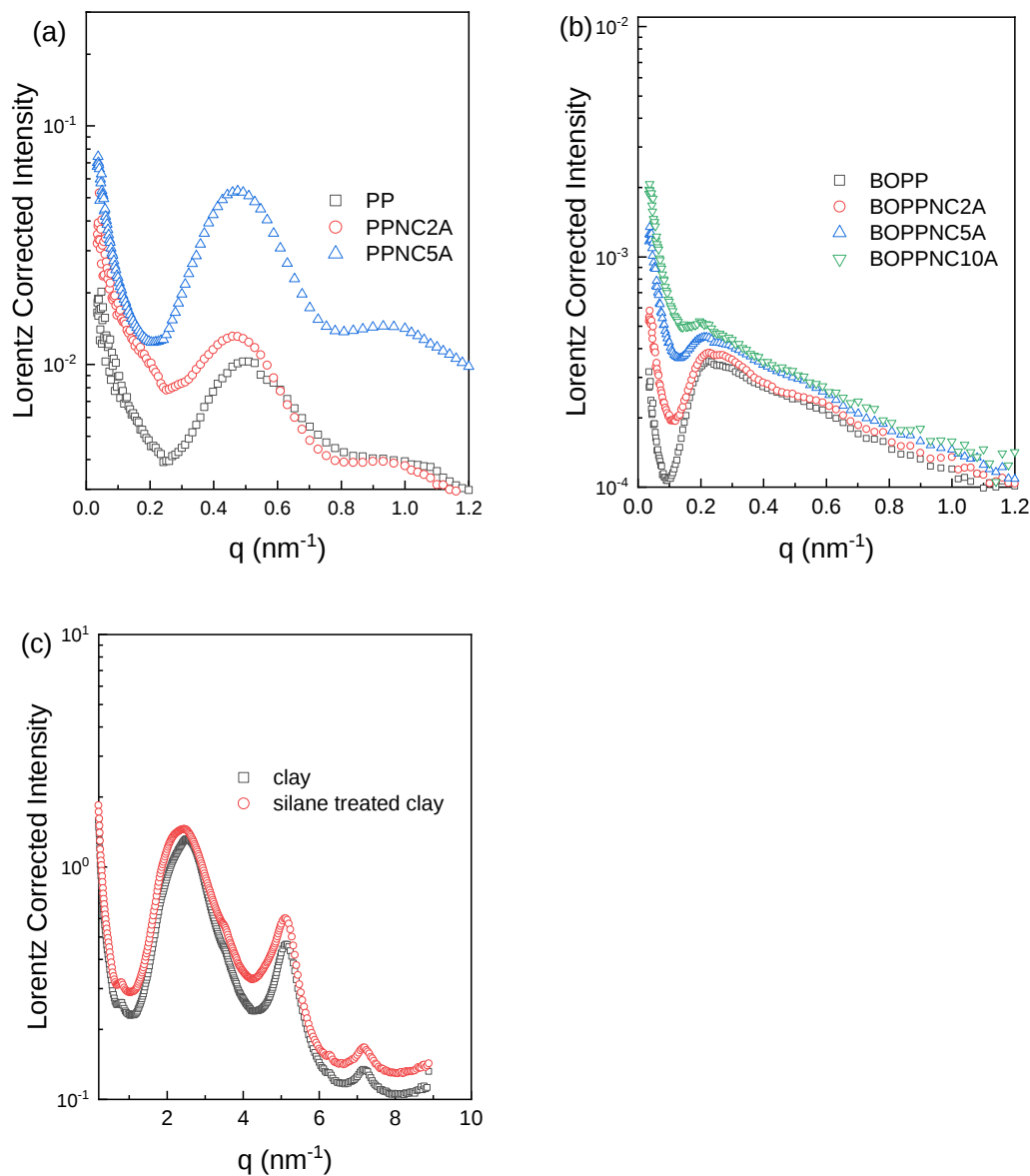


Figure 3.8 1D SAXS intensity profile of PP, nanocomposites and clay (a) Extruded (b) Biaxial stretched (c) Clay.

In order to quantitatively understand the structural evolution of these crystalline lamellae, dimensional parameters need to be characterized. Long period L_p , lamellar thickness L_c , Amorphous thickness L_a , and lateral dimension D has been used as important dimensional parameters to describe a lamellae crystallite as shown in Figure 3.9 Schematic illustration of dimension parameters to describe a lamellae crystal

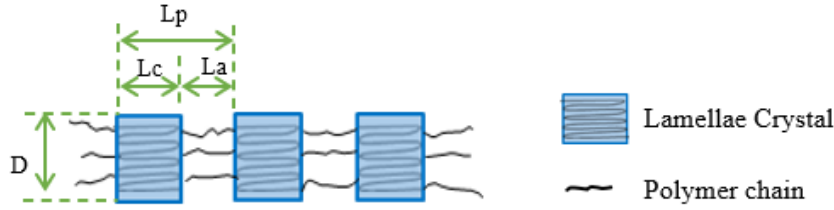


Figure 3.9 Schematic illustration of dimension parameters to describe a lamellae crystal.

The long period information could be obtained according to the peak position in 1-D SAXS curves. The long period of the lamellae was determined as below:

$$L_p = \frac{2\pi}{q_m} \quad (3.3)$$

Where q_m is the scattering vector of the peak. The lamellar thickness L_c and amorphous thickness L_a could be calculated based on long period L_p , crystallinity X_c and density ρ as follows:

$$L_c = \frac{X_c L_p \rho}{\rho_c} \quad (3.4)$$

$$L_a = L_p - L_c \quad (3.5)$$

$$\frac{1}{\rho} = \frac{X_c}{\rho_c} + \frac{1 - X_c}{\rho_a} \quad (3.6)$$

Where ρ_c (0.936 g/cm³) and ρ_a (0.854g/cm³) is the density of PP crystalline phase and amorphous phase respectively. Since the crystallinity in both PP and PPNC after biaxial stretching, the change of long period and lamellar thickness follows the same trend.

The lateral dimension, i.e., the average crystallite size was estimated from measurements of the full width half maximum (FWHM) $\Delta(2\theta)$ of corresponding WAXD diffraction peak. The Scherrer relation [129] was used to calculate the crystallite dimension in

the direction the crystal plane as below:

$$D_{hkl} = \frac{K\lambda}{\Delta(2\theta) * \cos\theta} \quad (3.7)$$

where K denotes a crystallite form coefficient, and λ denotes the wavelength of the incident X-ray. Even though this relation neglects lattice distortions which can lead to peak broadening, it can provide reasonable comparisons. Crystallite size has obtained via WAXD to investigate the structural evolution in drawn polypropylene [130] and Capt et al. [26] further suggested using D_{040} crystallite size to probe the evolution of crystal structure in a BOPP process. Specifically, this dimension could be used to estimate the average lateral dimension of in-film-plane oriented lamellae or crystallite, which has also been illustrated in Figure 3.10.

The lamellar thickness and lateral dimension before and after biaxial stretching have been summarized in Figure 3.10 (a) and (b), respectively. By comparing the Figure 10a and 10b, it can be inferred that after biaxial stretching, the lamellar thickness L_c increased in both unfilled and filled samples. This change could be attributed to the large strain-induced recrystallization of amorphous chains which may potentially grow on the fragmented crystal or bringing adjacent pieces. Furthermore, addition of nanoclay increased lamellar thickness L_c in all nanocomposites regardless of before or after stretching. This could be associated with increased recrystallization and lamellae thickening from increased nucleation provided by improved dispersion of nano layers after biaxial stretching. Causin et al. [131] also pointed out that nano-dispersed clay particles lead to an increase in long period of lamellae due to depressed equilibrium melting temperature and enhanced crystallization rate to ease chain folding. Such effect is even more magnified with exfoliation of clay, which also benefits from biaxial orientation as revealed above.

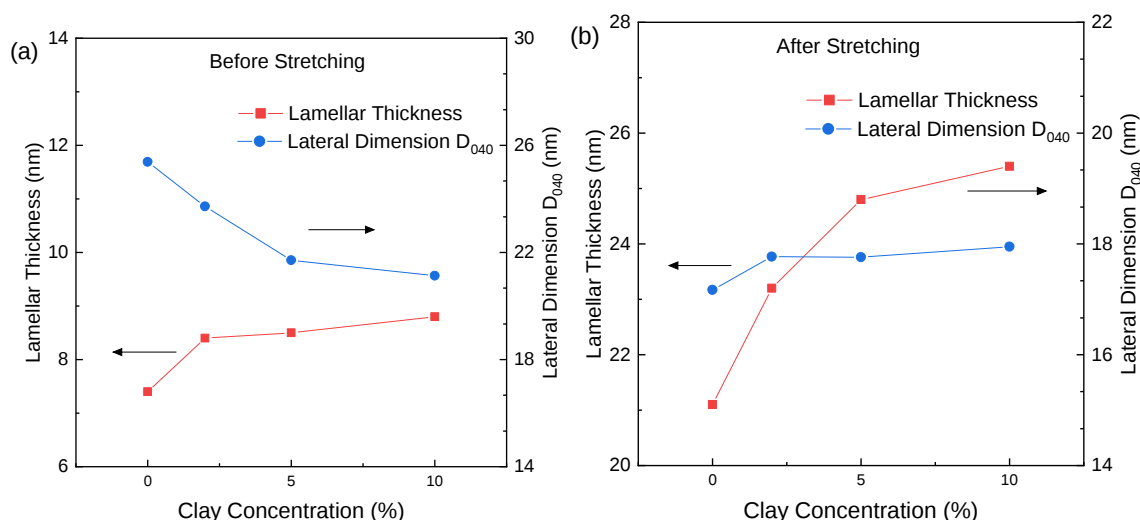


Figure 3.10 Lamellar thickness and lateral dimension D_{040} of PP and PP nanocomposites (a) before stretching and (b) after stretching.

It is also evident that D_{040} decreases significantly after biaxial stretching suggesting thicker lamellae becomes thinner. The decrease results from destruction of the original lamellar crystallite. There is no significant difference in final crystallite lateral dimension despite the smaller initial dimension in extruded nanocomposites. This may be explained by delayed onset of crystallites fracture to a higher stretching ratio. R.Rane et al. [132] reported that the existence of talc particles in PP-talc composites could preserve the existence of crystalline domains up to a higher draw ratio compared with neat PP in a solid phase die-drawing process. The remaining crystallite size may also account for the maintained yield stress. Rettenberger [24] et al. suggested such connection between crystallite size and yield stress in uniaxially stretched PP films. Overall, addition of nanoclay maintained PP oriented crystal structure after biaxial stretching.

Together with WAXD and SAXS, we could draw the scheme that original lamellae in extruded sheets eventually transfers into longer and thinner stacks of lamellae via crystal fragmentation and recrystallization. Figure 3.11 depicts the crystal structure evolution form

thickness-plane (MD-ND) view. Addition of nanoclay promoted these lamellae become more longer and thinner. From 2D SASX pattern, it could be inferred these smaller lamellae forms an in-plane uniformly distributed fibrous network.

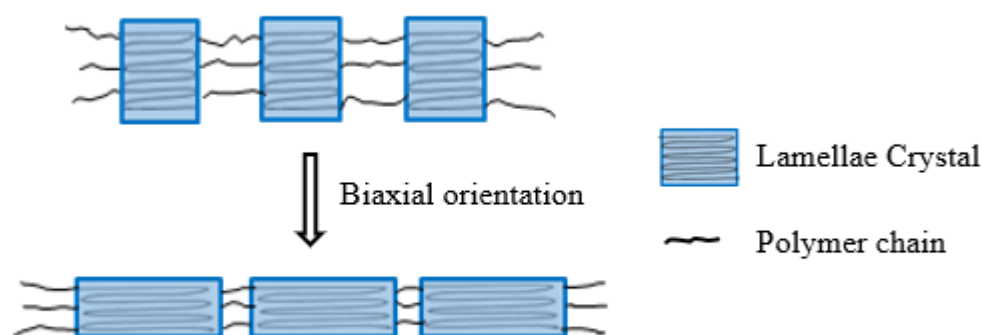


Figure 3.11 Schematic illustration of crystal structure evolution in biaxially oriented films (MD-ND plane).

3.3.5 Mechanical property

Mechanical properties obtained in both MD and TD for biaxially oriented nanocomposites and neat BOPP films from tensile tests have been summarized in Figure 3.12. Biaxial orientation process give rise to a remarkable increase in tensile modulus of base PP from 1.4 GPa to 3.4 GPa in BOPP. This is attributed to increased orientation of polymer chains by virtue of 7*7 high area stretching ratio. With addition of nanoclay, the modulus of BOPPNC was further increased up to 4.3 GPa. Tensile modulus depends primarily on the “fixed phase” represented by crystalline region and clay nanolayers in nanocomposites. The trend of higher modulus in MD in all cases could be correlated with pre-stretching in the extrusion process. The enhanced tensile modulus did not come at the expense of tensile strength as also shown in Figure 12. Moreover, the elongation to break was slightly improved in MD for nanocomposite film. There is no yielding pattern present in both the MD and TD tensile test profile. Similar

result has also been reported by A.J. DeVries et al. [133] The absence of yield is probably due to the fully stretched polymer chains at this large area stretching ratio,

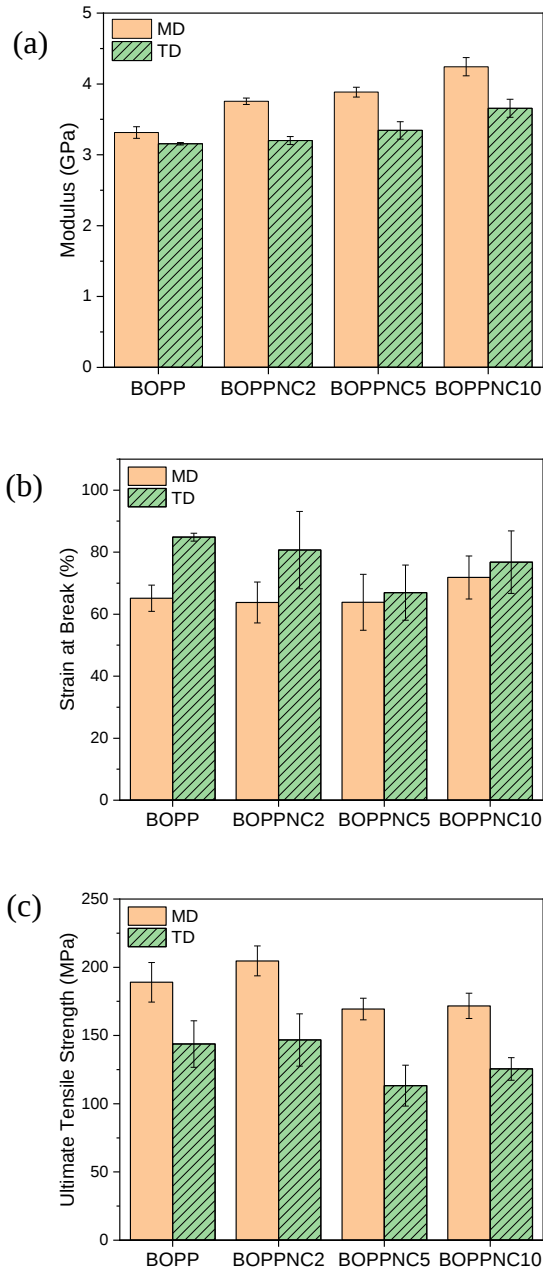


Figure 3.12 Mechanical properties of Biaxial Orientated PP and nanocomposite Films (a) Modulus; (b) Strain at break; (c) UTS.

The dashed diagonal line in Figure 3.13 represents the ideal equal balance in MD/TD. Compared with BOPP, all nanocomposite films distributed closer to the diagonal line indicating an improved in-plane isotropy. BOPPNC5 being the closest could be correlated to its dispersion extent. A similar trend of more balanced MD/TD elongation to break was also reported for nanocomposite blown film and was considered to correlate with cross-hatched lamellae formation [134]. With a much higher area stretching ratio in biaxial orientated films compared with blown film, the improved in-plane isotropy in nanocomposite film plane was maintained. The more balanced MD-TD elongation to break in the nanocomposite film could be explained by the more uniform distribution of in-plane oriented lamellae as shown in more isotropic 2D SAXS ring pattern

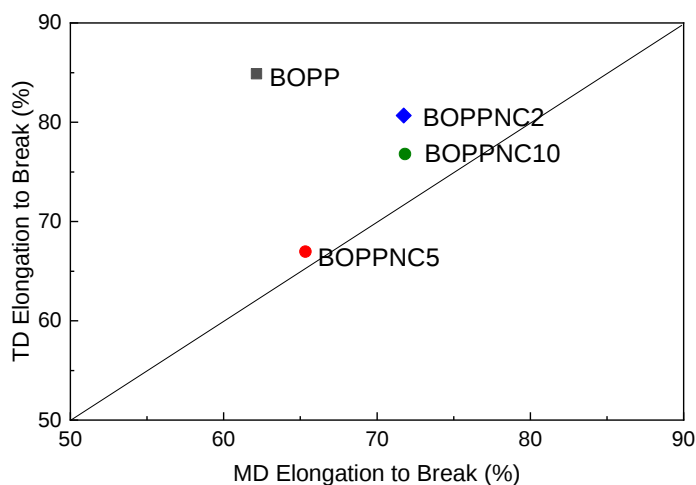


Figure 3.13 Elongation to break in TD versus MD in all biaxial oriented films.

3.3.6 Barrier property

The results for oxygen permeability (OTR) of biaxially stretched films at a calibrated 1-mil thickness have been summarized in Table 4. The presence of nanoclay also decreased both oxygen and water vapor permeability remarkably at all clay concentrations in this experiment. It has been reported barrier property could be limited or even deteriorated with

high concentration of clay during to either particle agglomerated tactoids [92] or cavitation occurred during processing [98]. The continuous reduction in our nanocomposite validated its processing and dispersion efficiency by virtue of attainment of sufficient anchoring up to 10wt% clay loading. The enhancement in barrier property indicated the effectiveness of impermeable nanoclay platelets not to mention that PPgMA has a higher affinity to polar molecules [135].

Table 3.4 Oxygen permeability of extruded sheets before stretching and biaxially oriented films after stretching.

	Extruded Sheets				Biaxially Oriented Films			
	PP	PP NC2	PP NC5	PPN C10	BOPP	BOPP NC2	BOPP NC5	BOPP NC10
Oxygen permeation rate through 1mil thickness (cc.mil/m²day)	3831.7 ±1.5%	3161.3 ±0.6%	2893.4 ±1.7%	2565.3 ±1.8%	1825.8 ±3.2%	1403.4 ±1.2%	1021.2 ±4.8%	826.2 ±5.5%

Water vapor permeability (WVTR) of these films is also summarized in Table 5. The fact that WVTR is also reduced with increased clay content further ascertained that nanoclay has been largely attached with PP chains overwhelming the potential affinity between clay particle and water molecules.

Table 3.5 Water vapor permeability of biaxially oriented films after stretching.

	Biaxially Oriented Films			
	BOPP	BOPP NC2	BOPP NC5	BOPP NC10
Water vapor permeation rate through 1mil thickness (g.mil/m²day)	3.2 ±4.7%	2.6 ±1.5%	2.1 ±6.6%	1.9 ±9.5%

Additionally, OTR was also measured for extruded sheets for comparison as shown in Table 3. It is readily evident that biaxial orientation process reduced oxygen permeability tremendously which was attributed to increased crystallinity and crystalline orientation. Figure 3.14 compares the relative reduction for each nanocomposite before and after biaxial stretching. The unfilled referenced value was calculated based on the portion and permeability value of neat PP and PPgMA in unstretched and biaxially stretched state [98] respectively. The extent of reduction at same loading of clay additive, i.e., BOPPNC with reference to BOPP, PPNC with reference to PP, was more pronounced after biaxial stretching. Since there is no significant difference in crystallinity in BOPP and BOPPNC after a dominating high strain stretching as indicated by WAXD in the next section, this augmented reduction must be correlated with the promoted degree of nanolayer orientation and delamination induced by biaxial orientation as confirmed by both TEM and shear rheology. The highest difference before and after biaxial stretching occurring at 5wt% clay concentration also corresponds consistently with the highest dispersion level achieved in BOPPNC5.

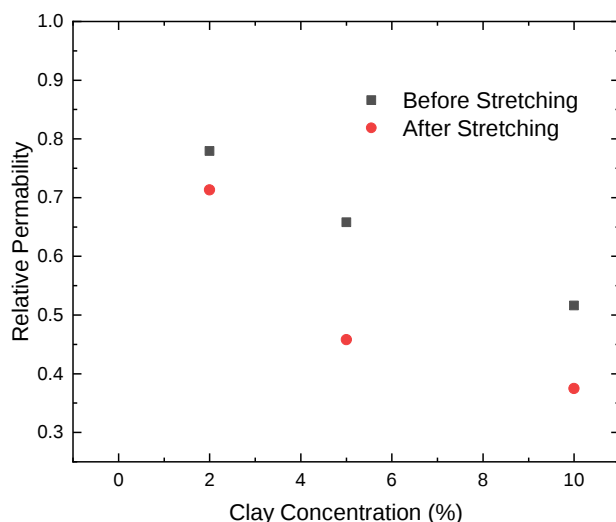


Figure 3.14 Relative oxygen permeability before and after biaxial stretching.

Schmidt et al. [136] has compared various commonly used models to describe barrier properties of polymer/2D filler nanocomposite utilizing a model system. The applicable range of each model has been validated and the influence of actual layer orientation was emphasized. A generic permeation equation was proposed as follows:

$$\frac{P_0}{P}(1 - \varphi) = 1 + \tau \left(\frac{2}{3} \right) \left(s + \frac{1}{2} \right) \quad (3.8)$$

Where P_0 and P is permeability of polymer and filler polymer respectively, φ is the volume fraction of inorganic filler, τ is geometric tortuosity factor depending on the inorganic filler dispersion, s is the orientation parameter. At relative low filler concentration, τ is taken as $\alpha\varphi/2$. In the ideal case where all impermeable nanofillers are oriented perpendicular to the diffusion direction, which is applicable in these highly stretched films, the orientation factor was taken as 1. The value of orientation parameter varies from -0.5 to 1. A value of -0.5 represents the condition of platelet nanofillers oriented parallel to the gas penetration direction and 1 corresponds to platelet nanofillers orientation perpendicular to the gas permeation direction. The experimental relative oxygen permeability and the model-predicted values based on nanoclay aspect ratio and concentration were compared in Figure 3.15. The experimental value shows high consistency with model prediction, especially at 2% and 5%. They show the similar trend of reduction with increasing clay concentration. This corresponds well to clay dispersion level as discussed above. It also approves the assumption of orientation factor equals 1 is reasonable which correspond to the ideal orientation of nanoclay platelets perpendicular to the permeation direction in these biaxially oriented nanocomposite films. A small deviation was observed at the highest clay concentration, which may be due to two possible reasons: 1. At concentration of 10wt%, the tortuosity factor $\alpha\varphi/2$ reaches applicable range limit 2. the effect

of nanoclay is dominating in lower concentration and at higher concentration the effect in matrix permeability due to the change of “aspect ratio” of these in-plane oriented lamellae in biaxially oriented nanocomposite film need to be considered.

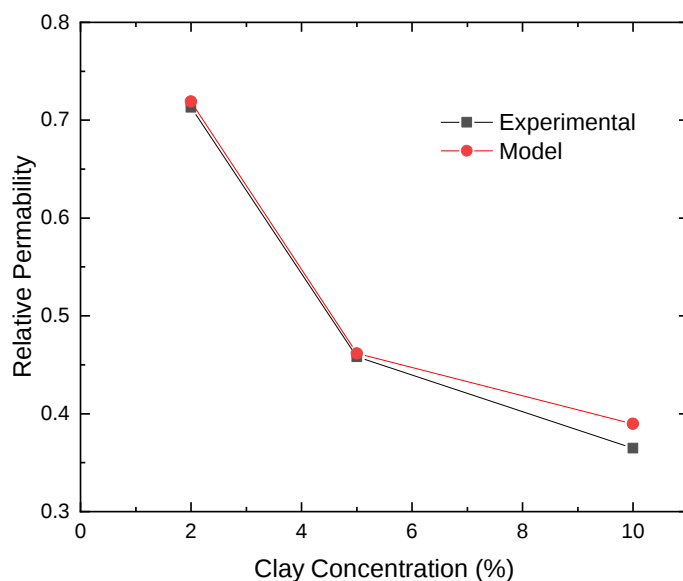


Figure 3.15 Comparison of relative oxygen permeability between experimental and model prediction.

3.4 Conclusion

Here we demonstrated a success in obtaining biaxially oriented polypropylene clay nanocomposite film with an area stretching ratio of 7×7 with nanostructured masterbatch additive. The resulting BOPPNC film exhibited high clarity as base BOPP. TEM and shear rheology revealed that nanoclay was well dispersed in the nanocomposite and more importantly, biaxial stretching further promoted the dispersion state of clay nanolayers with partial exfoliation. A high degree of in-plane orientation of nanoclay was also introduced by biaxial stretching. WAXD and SAXS revealed that the original lamellae were transfer in to longer and thinner stacks after biaxial stretching. Addition of nanoclay further increased the long period and the lamellae thickness of these lamella crystallite. 2D SAXS indicated a more

isotropic pattern in BOPPNC film compared to BOPP. BOPPNC film showed increased tensile modulus in both MD and TD with a more balanced elongation to break ratio, which could be correlated with improved in-plane crystalline orientation as observed by WAXD and 2D-SAX pattern. Both oxygen and water vapor barrier were significantly improved after biaxial orientation and further improved in BOPPNC film. The extent of improvement in oxygen barrier between unfilled and filled samples was more pronounced after biaxial stretching, which is attributed to further improved nanolayer exfoliation and orientation during the biaxial stretching process.

Chapter 4. Comparison of Simultaneous and Sequential Biaxially Oriented Polypropylene Nanocomposite Films

4.1 Introduction

Biaxial orientation has been developed as mainstream technique to produce most of transparent barrier packaging films [3,5]. During this process, a precursor specimen is stretched in two perpendicular directions to produce a thinner film. This usually occurs at semi-solid state below the melting temperature. The high stretching force causes a change of microstructure with more effective alignment of polymer chains following particular direction and such molecular orientation impart the stretched film with conspicuously enhanced performance such as optical transparency, mechanical robustness, and gas barrier [3]. These significant improvements were not attainable compared to conventional uniaxial stretching or sing-step process such as single bubble blown film. Of these biaxially oriented polymers, biaxially oriented polypropylene, BOPP, is one of the primary segment due to its low density, good modulus and low cost. In addition to packaging film, BOPP was also widely in other application such as insulation film, transparent film for display, laminated film, labelling film, shrinkable film, dielectric film, and separator film [4–10].

In industry, BOPP are mainly produced by two techniques: tenter frame and double bubble. These two processes represent two modes of biaxial orientation: simultaneous stretching and sequential stretching. The former is a one-step process where the specimen is drawn along two perpendicular directions, machine direction (MD) and transvers direction (TD), at the same time. Double bubble process is considered as simultaneous biaxial stretching. On the other hand, sequential stretching involves two steps. First the material is stretched along MD where its length is increased, and thickness is reduced effectively while the width is kept

at constant. In the second step, the MD-stretched film is stretched in perpendicular TD where its width is increased, and thickness is further decreased while the length is maintained. The processing parameters including strain, strain rate and temperature also varies. Accordingly, for BOPP, a typical area stretch ratio encountered in tenter frame line is approximately 5×7 while in double bubble process it is 6×6 [3].

Processing and structural development of BOPP has been of great interests in both academia and industrial as it is essential to understand the deformation behavior and structure evolution which determine the final property. In biaxial orientation process, the major variables include deformation mode (simultaneous or sequential) as well as stretching temperature and strain rate within each mode. Simultaneous or sequential biaxial orientation has been extensively studied either individually or together [33–37]. Lin et al. [33] investigated simultaneous and sequential BOPP with various balanced and unbalanced draw ratios. They indicated that sequential stretching led to a slightly lower density than simultaneous stretching with same draw ratio. Moreover, sequential stretching produced lower orientation in the first stretch direction and higher orientation in the second stretch direction compared to simultaneous stretching. Lüpke et al. [34] investigated sequential biaxial drawing of polypropylene films with various transverse draw ratio. The first MD stretching transforms the initially spherulitic morphology of the cast film into a stacked lamellae morphology (shish kebab) by partial melting which is then deformed after second TD stretching into a fibrillar network under the action of crystallographic slip processes ((010)[001] and (110)[001] slip). Further deformation orients the fibrils towards the actual draw direction. Uejo and Hoshino [35] compared both simultaneous and sequential biaxially stretched polypropylene film and they found three kinds of crystal orientation during biaxial orientation: 1) c-axis along the

stretching direction; 2) b-axis normal to the plane of the film; 3) [110] vector weakly normal to the film. They proposed a deformation model in simultaneous biaxial orientation, the structural element was oriented parallel to the plane of the film with crystal b-axis oriented perpendicular to the plane of the film while in sequential stretching, the fibrillar structure is oriented comparatively parallel to the stretching direction which differs from simultaneous stretching where a random orientation was suggested. Nitta et al. [36] also indicated that in sequential biaxial, the lamellar cluster blocks were orientated along first stretching direction and then rotated to the second stretching direction, which differs from simultaneous biaxial stretching where the crystalline lamellae rotate toward an in-plane alignment. Some other researchers also compared biaxial stretching to uniaxial stretching, and they have drawn similar conclusion that polymer chains tend to be more oriented in the plane of the film during simultaneous stretching while the due to the nature of two orthogonal stretching force[35][38][39]. After high stretching ratio, the initial crystalline morphology before stretching will transform to fibrillar structure after stretching [35].

In addition, the effect of stretch temperature and strain rate is also investigated [18,24,26,32]. It is found that decreasing strain rate or increasing temperature leads to a shift from the ductile to the quasi-rubber-like in biaxial deformation behavior of polypropylene. The deformation homogeneity is also affected. Moreover, the stretching temperature was found to be more dominating parameter in determining the films' behavior [30]. This is assumed owing to the degree of undermelting [31].

On a broader perspective, biaxial deformation behavior is not only encountered during biaxial oriented films, but also is an inevitable result of free surface molding process such as thermoforming or injection stretch blowing molding in manufacture of thin-walled packaging

containers. During these processes, polymer materials are heated and subjected to rapid biaxial deformation as they are drawn into the shape of a mould. This could be quite complex due to the fact that processing parameters such as direction of strain, strain rate, temperature can vary significantly according to the eventual application, part location or processing stages. For example, it is considered simultaneous biaxial stretching occurs in the base of a formed product while sequential biaxial stretching occur during stretching plug-air or stretching rod-air stage [16]. For process simulation and optimization, it is critical to accurately measure the material biaxial deformation behavior under appreciate parameters. Motivated by this, increasing numbers of studies emerged focusing on the biaxial deformation under variable processing conditions for simulation and prediction of thermoformability [16,107,109].

Barrier property is of particular value for BOPP with its prevalence in packaging industry. Improve the barrier performance has always been demanding and polymer nanocomposites incorporating nanoparticles such as nanoclay have gained immense research attention as a facile approach [57]. It is well recognized that nanocomposite will exhibit enhanced barrier properties by creating a tortuous path which will decelerate the diffusion of gas molecules through the matrix. To achieve significant performance enhancements, good dispersion of the nanoclay in the matrix and thermodynamic compatibility between the organoclay and the polymer are required. Polymer nanocomposites can be prepared by in-situ or melt-mixing methods. While in-situ polymerization usually yields better dispersion of clay platelets than melt-mixing, the latter approach is more economical and environmentally friendly.

However, it is quite challenging when nanocomposite incorporating nanoclay is subject to biaxial deformation. Either biaxial orientation film process or thermoforming process

involves a large deformation of the preform. Presence of nanoparticles adds rigidity, abates stretchability and therefore the nanocomposite is more prone to early failure specially under high stress [97,98]. As a result, there has been limited work reported on biaxially orientated polymer clay nanocomposite film especially polypropylene-clay nanocomposite film [39,54,103]. Abu-Zurayk et al. [103] investigated the equi-simultaneous biaxial deformation behavior and mechanical properties of polypropylene nanocomposite melt blended with 5wt% montmorillonite clay. They demonstrated that the presence of clay increases the yield stress relative to the unfilled PP at typical processing temperatures and that the sensitivity of the yield stress to temperature is greater for pp nanocomposite. The stretching process is also found to have a significant effect on the delamination and alignment of clay particles and on yield stress and elongation at break of the stretched sheet. However, the maximum area stretch ratio was 3.5×3.5 as indicated in their work which fall behind industrial et al. requirements. Furthermore, there is no comparative study between simultaneous and sequential stretched nanocomposite film and a lack of comprehensive study covering the processing, structure and property relation.

A recent effort exhibited superb reinforcing effect in promoting the interaction between pp matrix and organoclay [74,75,89]. The vapor phase silane treatment of organoclay provides enhanced silane penetration into the interlayer via reactive coupling galleries which in turn enhanced interfacial adhesion and improved nanoparticle dispersion in pp matrix when coupled to high-molecular weight functionalized compatibilizer. As a consequence, improved melt strength and modified rheological behavior was observed. This promotes nanocomposite processability in application such as foaming and blown film. A successful simultaneous biaxial stretched nanocomposite film was also confirmed which provide prerequisites for this

research.

To conclude, understanding the biaxial deformation behavior under different processing conditions not only help with pilot trial for commercial biaxial oriented film process such as tenter frame and double bubble, but also important for modelling thermoforming or stretch blow moulding process. Given the lack of research in biaxially oriented polymer nanocomposites film especially for melt processed polypropylene clay nanocomposite, it is therefore of significant interest to investigate how the material response to different deformation mode, i.e., simultaneous and sequential biaxial stretching under appropriate parameters. In this work, PP clay nanocomposite was prepared from masterbatch additives incorporating silylated organoclay and a maleated propylene compatibilizer and then biaxially stretched via a KARO IV biaxial stretching apparatus at conditions mimicking industrial manufacturing. The effect of stretching modes as well as the processing parameters including stretching rate and stretching temperature on the stress-strain response during the biaxial stretching process was investigated. The crystal morphology, optical transparency, mechanical and barrier property of both simultaneously and sequentially biaxial stretched nanocomposite film was compared. In addition, oriented film via the laboratory stretcher was compared to the film from a commercial production line. The present findings provide important guidance for determining the optimum processing parameters and controlling the final film structure depending on the end-use application.

4.2 Materials and Characterization

4.2.1 Materials

Two polypropylene grades were used in this work. PP526P, supplied by Sabic (MFI 8.0, ASTM 1238; density=0.90 g/cm³), was used as major material. PP4792, supplied by

ExxonMobil (MFI 2.7, ASTM 1238; density=0.90g/cm³), was used as in the supplemental work to investigate the effect of biaxial stretching temperature. The maleic anhydride-grafted PP (PPgMA) compatibilizer grade was Exxelor PO-1015 supplied by ExxonMobil, which is a random copolymer with ethylene (M_w = 123,000; 0.42wt% bound maleic anhydride). Organically modified montmorillonite Nanomer I.44P was obtained from Nanocor, which has a quaternary ammonium ion surfactant with two octadecyl tails. The reactive silane coupling agent was Dynasylan 1411, an aminoalkyl dimethoxysilane from Evonik.

4.2.2 Nanocomposite preparation

The silane treatment was conducted via a solvent-free process at Malvern Minerals Co. where the organoclay was exposed to a 0.8wt% refluxed silane vapor. This silane concentration was pre-determined as the optimized level for sufficient coupling. The treated organoclay was then sieved with a No. 200 mesh. Nanocomposites incorporating PP, PPgMA, and treated organoclay were compounded in a Leistritz twin screw extruder (diameter = 27 mm; L/D = 48) at 180 °C and RPM = 200. Before compounding, the PPgMA and grafted organoclay were dried in vacuum oven to remove moisture. A two-step compounding process involving a masterbatch and “let-down” was utilized. The masterbatch contained 1:1 clay: PPgMA concentration ratio and comparable loading of base PP to improve the mixing. The “letdown” was then made by adding masterbatch to PP homopolymer to prepare nanocomposites with various clay loadings. The final composition of nanocomposites was presented in Table 4.1. Precursor sheets for biaxial orientation were prepared in a single screw sheet extrusion line.

Table 4.1 Compositions of PP/clay nanocomposites.

	Polymer matrix	Amount of clay (wt%)	PPgMA to clay ratio
PP	PP (MFI 8.0)	0	1:1
PPNC5	PP (MFI 8.0)	5	1:1
PP-E	PP (MFI 2.0)	0	1:1
PPNC5-E	PP (MFI 2.0)	5	1:1

4.2.3 Biaxial Stretching

Biaxially oriented PP and PPNC film was prepared on a Karo IV biaxial apparatus at Brückner, Siegsdorf, Germany. Square specimen (90 mm × 90 mm) was cut from the melt-extruded PP and PPNC precursor sheets with ~1.2 mm thickness. In the major work investigating the effect of stretching mode and stretching rate based on PP526P, the annealing oven as well as the stretching oven were held at 156 °C for obtaining partly molten state of PP. After preheating, the samples were biaxially stretched under a range of processing conditions. Forces and displacements were recorded during the stretching process and stress-strain curves were generated based on these data. A trial run was carried out first to probe the stretching possibility. In all cases, the stretching temperature was set at 156 °C. For simultaneous equal-biaxial stretching, the stretching rate was selected at 200% s⁻¹ and 400% s⁻¹. The final area stretching ratio of 7 × 7. For asymmetric sequential asymmetric biaxial stretching, the MD/TD stretching rate was selected as 200% s⁻¹ /200% s⁻¹, 400% s⁻¹ /200% s⁻¹, 400% s⁻¹ /400% s⁻¹, respectively. The final area stretching ratio 5 × 9. The different area stretching ratio in two the stretching modes was selected to mimic the practical values accounted in tenter frame and double bubble process. The final stretched PP and PPNC films were achieved with ~25microns

thickness and labelled as BOPP and BOPPN5, respectively. In the supplemental work to investigate the effect of stretching temperature, PP4792 was used. Only simultaneous equal-biaxial stretching was applied, and the stretching rate was kept at 50% s⁻¹. The annealing oven temperature was kept as equal to the stretching oven temperature which was selected at 150 °C and 155 °C, respectively. The final film thickness was ~9 microns.

4.2.4 Characterization

The uniformity and transparency of biaxially stretched films were initially judged by eye. A PerkinElmer Lambda-800 Ultraviolet-visible spectrometer was used for light transmission measurement from visible light range (400 nm to 700 nm) to quantify the clarity of biaxially oriented film. The thickness of the film was measured with a micrometer along MD from center to the edge of the film at a fixed interval. Repeated measurements were conducted not only to obtain more reliable results but also to check the film uniformity.

Small-angle X-ray Scattering (SAXS) was performed at Beamline 12-ID-B Advanced Photon Source of Argonne National Laboratory with the x-ray energy of 13.3 keV ($\lambda = 0.9347$ Å). The scattered x-ray intensities were measured using a two-dimensional (2-D) Pilatus 2M detector. The sample to detector distance was set to 2.0 m and the detecting range of the scattering wave vector $Q = 4\pi\sin \theta / \lambda$ ranges from 0.0035 to 0.9 Å⁻¹, where 2θ is the scattering angle. The method to determination of long period of the lamellae was described in Equation 3.3.

The cross section of biaxially oriented nanocomposite film is observed by JEOL-6610LV scanning electron microscope. The samples were cryogenically fractured after immersed in liquid nitrogen for 30 mins. The fractured cross-section is sputter coated with gold. SEM observation is conducted using an accelerating voltage of 12KV and spot size of

30mm.

The mechanical properties of oriented films were measured with an Instron 5565 universal testing machine using film fixture according to ASTM D638. A thin slice of 2.54 cm wide and 10 cm long was cut from the middle portion of the biaxial stretched films with a specialized cutting stage to minimize the rough edges which could lead to early fracture. Specimens from MD and TD were stretched uniaxially at ambient temperature and a strain rate was 50 mm/min until fracture. 1% secant modulus was calculated.

A Mocon Ox-Tran 2/21 unit was used for OTR measurements, and a Mocon Permatran-W 3/33 unit was used for WVTR measurements according to ASTM D3985. Both instruments were calibrated at 23°C with a standard film of known permeability provided by Mocon. The test specimens cut from middle portion of films were mounted and laminated with a 5cm² size aluminum mask provided from Mocon Inc. to reduce the exposed area. OTR measurements were conducted at 23 °C and 0% RH while WVTR measurements were conducted at 25 °C and 100% RH. Two specimens from the same film were tested to obtain the average permeability. All results are calibrated to a film of 1 mil thickness.

4.3 Results and Discussion

4.3.1 Biaxial stress-strain behavior

The stress-strain response of neat pp and pp nanocomposites along machine direction (MD) and transverse direction (TD) to the two biaxial deformation modes under the same stretching temperature (156 °C) and stretching rate (200 %⁻¹) has been shown in Figure 4.1, where (a) (b) (c) (d) records the stress-strain curves along MD in simultaneous stretching, TD in simultaneous stretching, MD in sequential biaxial stretching and TD in sequential biaxial stretching, respectively. First of all, it was apparent that at this typical processing window

under both deformation modes, both PP and PPNC could be stretched successfully to the desired stretching ratio along MD and TD without breakage. Consequently, the final area stretching ratio achieves 49 (7×7) in simultaneous equal biaxial stretching and 45 (5×9) in sequential biaxial stretching. As stated in the previous context, these ratios are critical in mimicking the stretching ratio accounted in industrial biaxial orientation process such as tenter frame and double bubble.

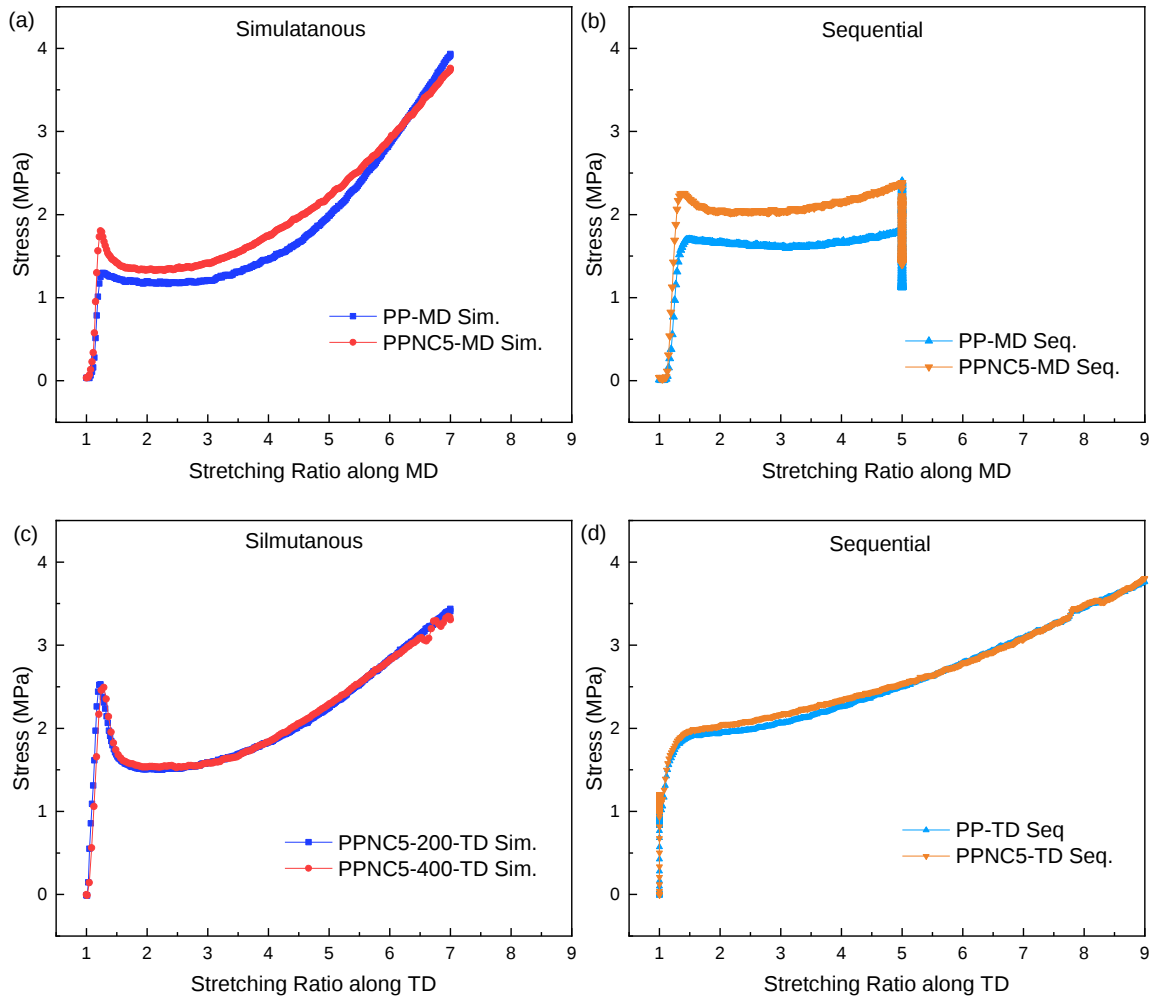


Figure 4.1 Stress-strain response of PP and PPNC5 during two stretching modes along different stretching direction: a). along MD in simultaneous stretching; b) along MD in sequential stretching. c). along TD in simultaneous stretching; d) along TD in sequential stretching. Stretching temperature is 156 °C and stretching rate is 200% s⁻¹ /200% s⁻¹ along MD/TD in all cases.

As shown in Figure 4.1 (a) and (c), during simultaneous biaxial stretching, the stress-strain curves of both PP and PPNC showed a typical ductile behavior. Both MD and TD curves showed an obvious initial yielding followed by softening plateau and a strain hardening. It is anticipated that in the precursor extruded sheet before biaxial stretching, there coexists partially aligned lamellae due to extrusion force and partially random-distributed lamellae inside spherulites. Upon stretching, multiple structure development process may occur: the spherulites were destroyed via crystal fragmentation and slip; the slightly aligned lamellae may also encounter either crystal slip or recrystallization growth; the amorphous chains will undergo recrystallization. The final crystalline morphology will be gradually transformed into fibrils along MD and TD at high strain. In addition, at early stage of stretching, i.e., at low strain, the stress levels along MD are slightly lower than TD at the same stretching ratio while TD curves showed a sharper early yielding point and higher yield stress. The softening plateau was also slightly wider along TD. However, at later stage of stretching, i.e., at high strain, the stress levels in MD are higher than TD with more significant strain hardening appearing. This phenomenon was associated with the pre-stretching in the precursor extruded sheet where the part of original crystal lamellae were slight aligned along MD.

As shown in Figure 4.1 (b) and (d), during sequential biaxial stretching, the stress-strain response profile was quite different when compared with simultaneous biaxial stretching. Along the first MD stretching step, the sequential stretching results in less sharp yield point. Compared to MD along simultaneous stretching, there is a much broader softening plateau after the yielding point which prolonged until the end of MD stretching. On the contrary, along MD in sequential stretching, no further increase in stress levels appears after the softening plateau and consequently no strain hardening behavior was observed. This is probably because the specimen is only subject

to a relative low MD draw ratio of 5, where the fibrillar structure has not been fully developed at this strain. Moreover, there is a significant rise in overall stress levels for a given stretching ratio compared to that along MD in simultaneous stretching.

On the other hand, during TD in sequential stretching, a lack of characteristic yielding point became more distinct. A rubbery trend in stress-strain response was observed where the stress rises more steadily with increasing strain. There is no softening plateau appears and the strain hardening behavior become less aggressive at higher strain. Similar to the comparison along MD between simultaneous stretching and sequential stretching, the stress levels along TD in sequential stretching at given strain were also considerably higher than that along TD in simultaneous stretching. The higher stress at given strain in sequential stretching than that in simultaneous stretching on biaxial oriented films has also been observed by other researchers [16][33].

The stress-strain response of only PP nanocomposites to changes in stretching rates is investigated in this part. Figure 4.2 (a) (b) (c) (d) summarizes the PPNC stress-strain curves along MD in simultaneous stretching, TD in simultaneous stretching, MD in sequential biaxial stretching and TD in sequential biaxial stretching, respectively. The temperature is fixed at 156 °C. Two strain rates were selected for simultaneous stretching: 200% s⁻¹ and 400% s⁻¹. Usually increasing strain rate will result in a stiffer response with increased stress levels. However, as shown in Figure 4.2 (a) (b), surprisingly the stress-strain curve of PPNC at stretching rate of 400% s⁻¹ is similar to that at 200% s⁻¹ along either MD or TD. Martin *et al.* [16], Buckley *et al.* [137], and Llana and Boyce [138] have also reported similar observations during biaxial orientation of PP or PET. They suggested this phenomenon generates from adiabatic heating effects when the heat generated owing to plastic deformation exceeds the

heat conduction rate from the material, which will cause an evitable temperature in the material. The temperature rise will cause increased polymer melting and softening. Such effects will become more prominent when the material is subject to very high deformation rate. In our case, at a temperature of 156 °C plus increased rigidity in PPNC, a strain rate of 400% s⁻¹ may cause a very high adiabatic heat generation exceeding the heat dissipative rate and thus result in a similar stress level as 200% s⁻¹.

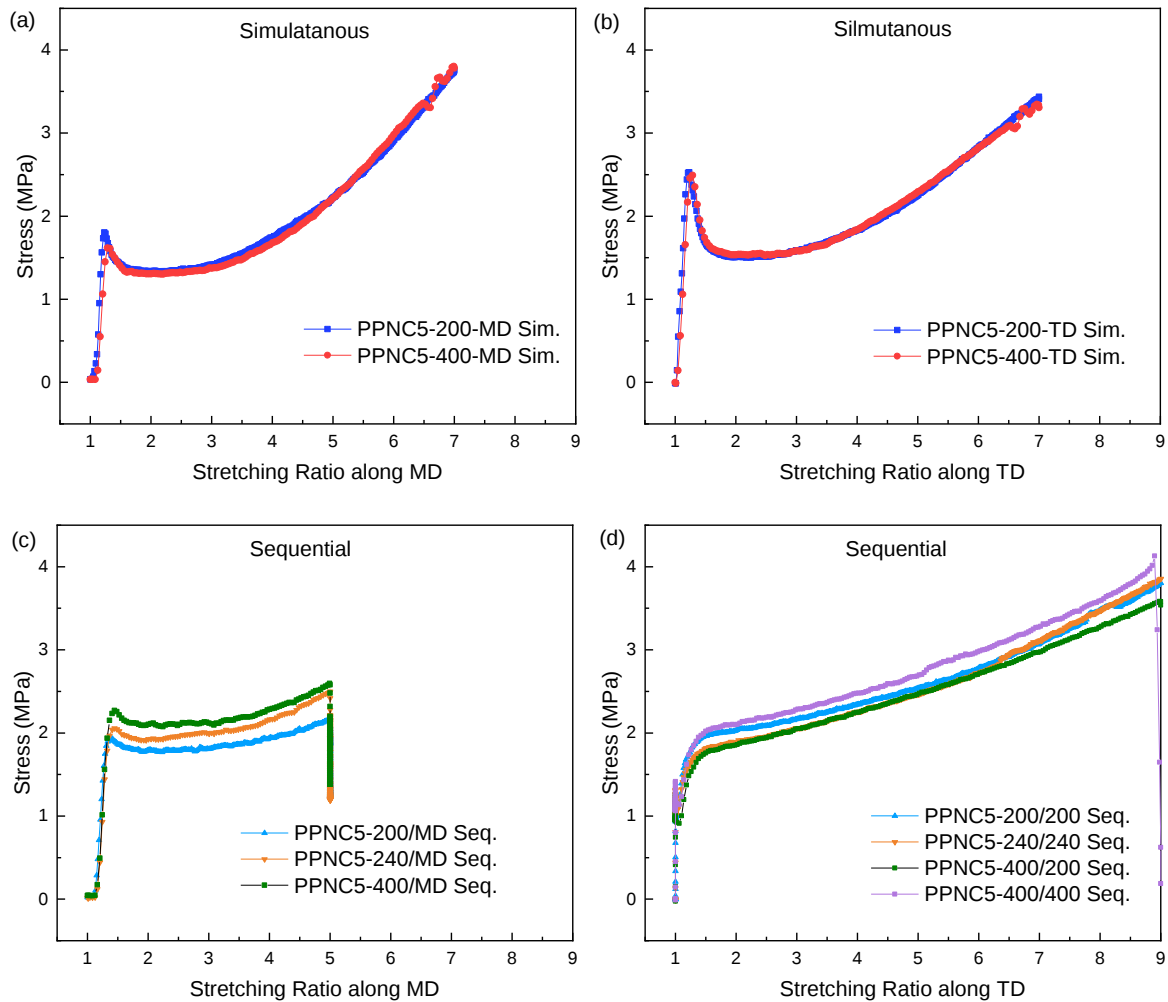


Figure 4.2 Effect of stretching rate on stress-strain behavior during biaxial stretching of PP and PPNC: a). along MD in simultaneous stretching; b) along TD in simultaneous stretching. c). along MD in sequential stretching; d) along TD in sequential stretching. Stretching temperature is 156 °C in all cases.

On the other hand, for sequential biaxial stretching, four speed profiles were selected as revealed in Figure 4.2 (c) (d): MD / TD stretching rate as $200\% \text{ s}^{-1} / 200\% \text{ s}^{-1}$, $240\% \text{ s}^{-1} / 240\% \text{ s}^{-1}$, $400\% \text{ s}^{-1} / 200\% \text{ s}^{-1}$, $400\% \text{ s}^{-1} / 400\% \text{ s}^{-1}$. These MD / TD rates were aimed to have a systematic comparison when the rate changed is individual or combined. Figure 4.2 (c) show that, during the first stretching step along MD, as the strain rate increases, the stress level of PPNC5-200/200, PPNC5-240/240, PPNC5-400/200 and PPNC5-400/200 also gradually increases with the last two are same since the MD strain rate is identical. This observation is as expected that increasing strain rate results in a stiffer response.

In the second stretching step along TD, by comparing PPNC5-400/200 to PPNC5-200/200, the stress levels were actually lower than that the former. This is due to the fact that the original crystals were oriented along MD in the first stretching step and the degree of orientation was higher with higher stretching rate which makes the initial TD strength in 400/200 at the beginning of second stretching step was lower than 200/200. By TD stretching these MD aligned crystal are gradually turned toward TD. Since the TD stretching rate is same, the overall stress levels are lower in PPNC5-400/200. This reason also explains the other two stretching behavior when compared to PPNC5-200/200. In PPNC5-240/240, the initial stress level was slightly lower due to slightly higher MD stretching rate but due to the higher TD stretching rate, the stress response exceeds PPNC5-200/200 at high strain. In PPNC5-400/400, the initial stress level was also lower but due to a much higher TD strain rate, the stress level already rises over PPNC5-200/200 at early stage of stretching.

The effect of stretching temperature on the stress-strain response during simultaneous stretching was investigated in this section. Two temperatures were selected: $150\text{ }^{\circ}\text{C}$ and $155\text{ }^{\circ}\text{C}$. A different grade of PP with lower melt flow index was used which has been demonstrated

in the experimental section. The precursor sheet was around 0.3 mm, and the final stretched films was about 8 microns. As shown in Figure 4.3 (a) (b), at two selected temperatures, both neat PP (PP-E) and PP nanocomposite with 5% clay loading (PPNC5-E) were successfully stretched to a ratio of 5.3×5.3 . Along MD, the increase in temperature causes a reduction in the stress drawn in both PP-E and PPNC5-E although the basic characteristic stays the same. By increasing the temperature from 150 °C to 155 °C, the stress levels for a given strain almost falls to approximately half of the original value. PP has been known to be highly temperature sensitive. Siegmann and Nir [30] reported that stretching temperature was found to be the dominating process parameter in determining biaxially stretched films' behavior. Along TD in simultaneous stretching, the stress-strain reponses of PP-E and PPNC5-E behaves in a similar fashion as MD. It is worth to mention as shown in Figure 4.3, there is an increased signal-to-noise ratio. This is due to the fact that the precursor sheet was thinner and thus the stretched film. The signal-to-noise ratio suggests that in practical biaxial orientation manufacturing, an optimal precursor thickness was also important in order to have better consistent products.

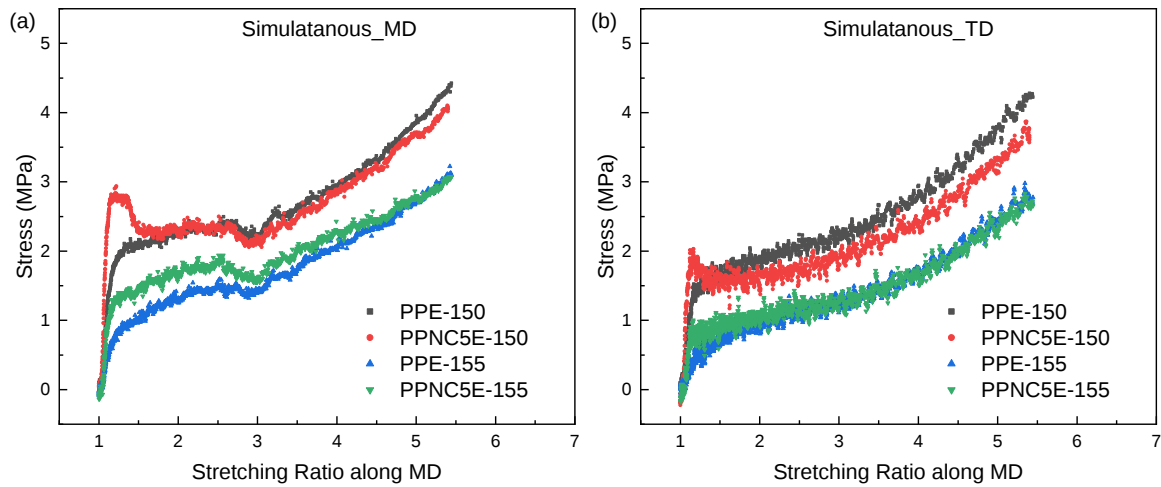


Figure 4.3 Effect of stretching temperature on stress-strain behavior during simultaneous biaxial stretching of PP and PPNC: a). along MD; b) along TD.

Combing Figure 4.1, Figure 4.2 and Figure 4.3, it can be concluded that regardless of the stretching modes and processing parameters, addition of silyated organoclay did not change the basic characteristic stress-strain behavior of neat PP. Generally, there is a rise in the overall stress levels in PPNC especially at low strain. This is expected since addition of rigid fillers cause an increase in system rigidity. The tensile modulus as well as the yield stress were found to be higher for the nanocomposite compared with neat PP. This could be attributed to the increased crystallinity and greater entanglement of polymer molecules due to the presence of clay nanoparticles.

While PP and PPNC behave in a similar fashion, the changes on the stress strain behavior caused by nanoclay in the two stretching modes were slightly different. Specifically, at low strain, in simultaneous stretching, PPNC exhibited increased rigidity with increased yielding along both MD and TD while in sequential stretching, addition of clay only introduce a more distinct yielding characteristic along MD but did not cause any significant change along TD. At particularly high strain, there is a crossover of PP and PPNC stress-strain curves along both MD and TD in simultaneous stretching. It is speculated this observation at was associated with further delamination and orientation of clay platelets at high strain stretching. On the other hand, such crossover is not observed in MD and TD in sequential stretching.

Again, incorporating inorganic fillers in polymer matrix usually leads to increased rigidity and thus decreased stretchability. In all cases, adding clay particles did not cause any early fracture. High area stretching ratio (7×7 in simultaneous biaxial stretching and 5×9 in sequential biaxial stretching) was successfully achieved in both neat PP and PPNC without breakage, which is significant for commercial biaxial stretching process. This result is evidence of enhanced interfacial interaction between clay particles and polymer matrix.

4.3.2 Stretched film appearance

For all the structure and property measurement in this section and after, only the films simultaneously and sequentially stretched under stretching temperature of 156 °C and stretching rate of 200% s⁻¹ /200% s⁻¹ along MD/TD were compared. At a initial glance, the films appear transparent and flexible. Both simultaneously and sequentially biaxial oriented BOPP and BOPPCNC films of ~25-micron thickness exhibited high clarity without any voids. This was confirmed by visual inspection as well as an optical microscope. The total transmittance measurements via a UV-Vis spectrometer have been presented in Figure 4.4. Both neat BOPP film and BOPPCNC film show high transmittance in the visible light range, i.e., from 400nm to 700 nm wavelength. The incorporation of 5 wt% clay nanolayers did not degrade light transmission significantly. To maintain high transparency, it is necessary to have obstacle particles with dimensions less than light wavelength to avoid light scattering. The overall high light transmission indicated that the nano-scale dimension of filled clay particle without aggregates as a result of enhanced dispersion and delamination. There is a trend of decreased transmittance of BOPPCNC in shorter wavelength range, which is due to the decreased difference between light wavelength and filler particle dimension. Overall, the simultaneously stretched film shows a higher transmittance value compared to sequentially stretched film of the same composition, which is probably due to the slightly higher area stretching ratio in the former.

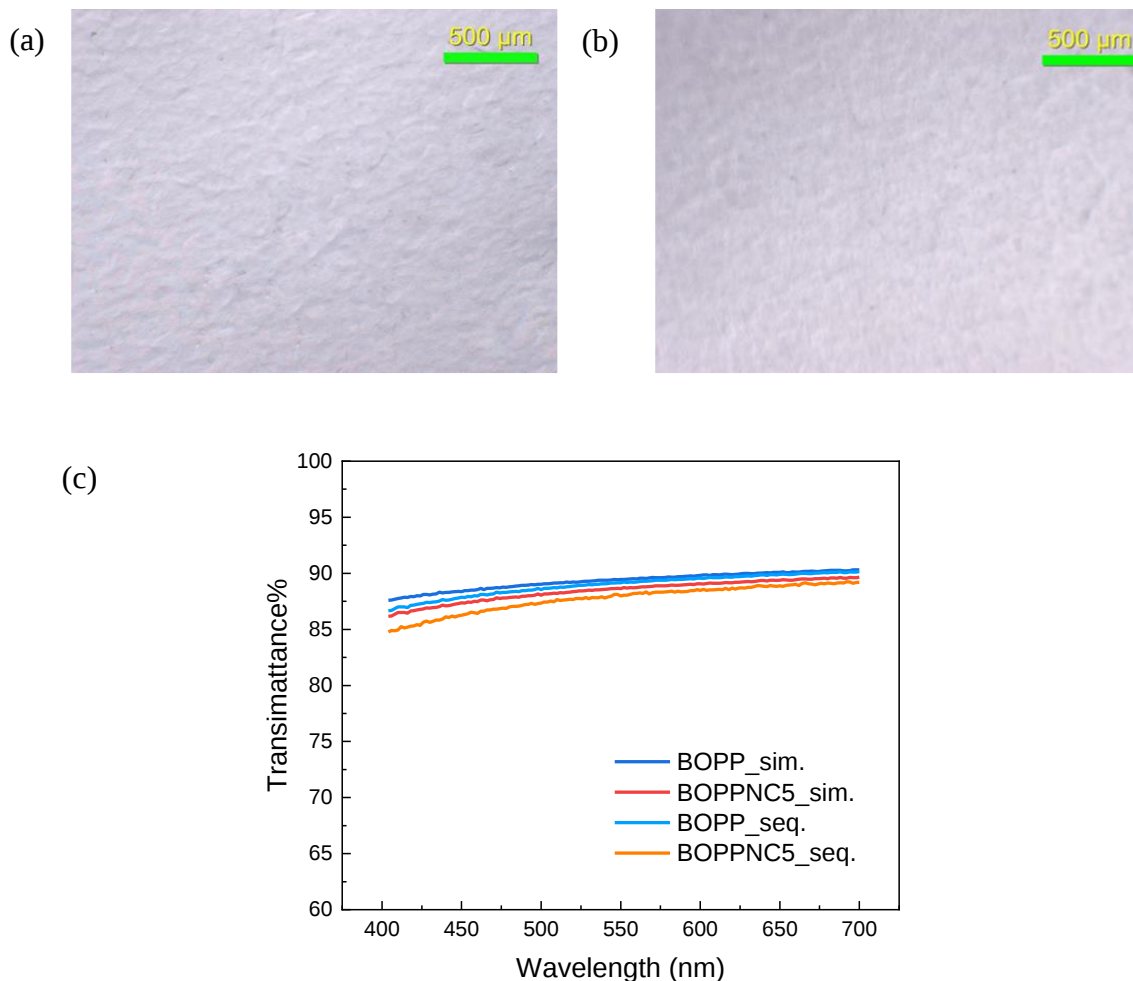


Figure 4.4 Optical performance of simultaneously and sequentially stretched film under stretching temperature of 156 °C and MD/TD stretching rate of 200% s⁻¹ /200% s⁻¹, top, microscopy image, (a)BOPPNC5_sim(b) BOPPNC5_seq; bottom, (c) Total transmittance.

The thickness profile from center to edges of all simultaneously and sequentially stretched films was measured by a micrometer. Figure 4.5 (a) (b) (c) (d) represent the thickness distribution along MD/TD of simultaneously stretched BOPP, simultaneously stretched BOPPNC5, sequentially stretched BOPP, sequentially stretched BOPPNC5, respectively. For all stretched films, there is an acute drop in film thickness at regions with distance of ~5 cm to the edges to the film. This is associated with the clamping of the films where these clipped regions are in “fixed” position. At distance > 10cm from the clamping points, all films exhibit

a highly consistent thickness profile in both stretching modes. Within these inner regions, simultaneously stretched films shows a higher thickness consistency between MD and TD compared to sequentially stretched films. Moreover, comparison between BOPP and BOPPNC5 under same stretching mode reveals that addition of nanoclay did not affect the thickness regardless of the stretching modes.

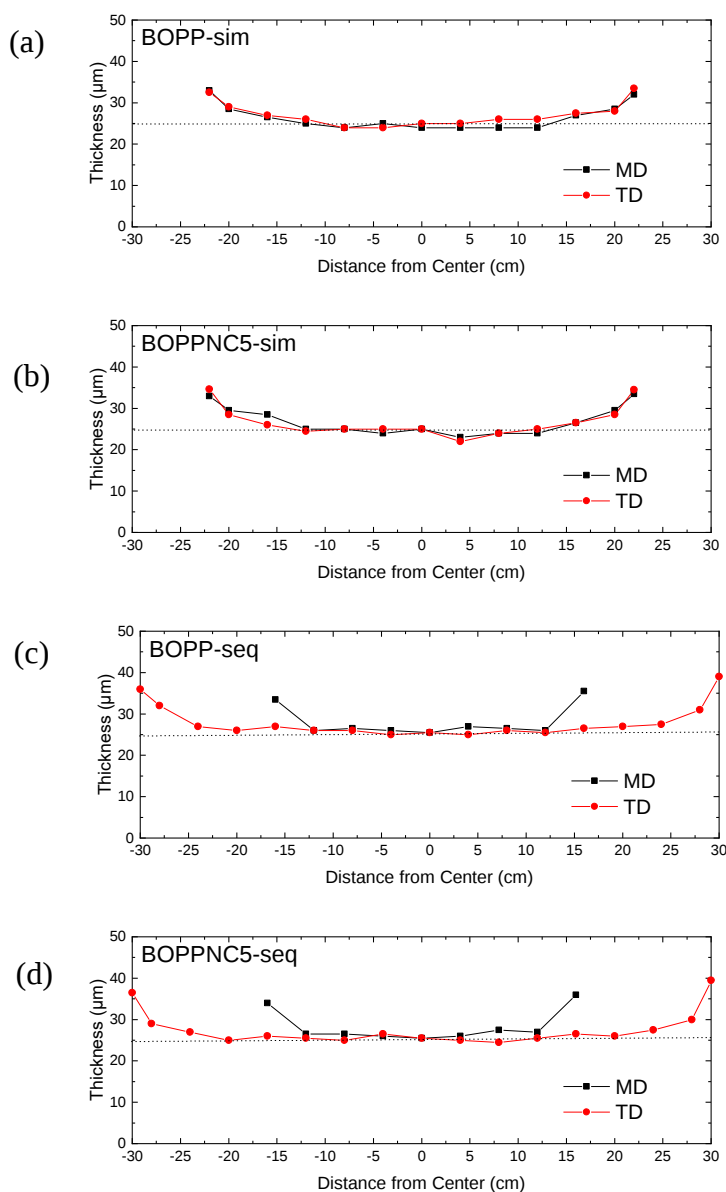


Figure 4.5 Thickness profile of biaxially stretched BOPP and BOPPNC.

Overall, the simultaneous equi-biaxial stretching process produces film with a more uniform MD/TD thickness profile across the film compared to the asymmetric sequential stretching process where the latter produces films with more uniformity along the long stretching TD direction due to the inherent unbalanced stretching ratio. Besides, the accomplishment of transparency and uniform thickness in BOPPPNC film under both stretching modes is critical for practical application.

4.3.3 SAXS

To investigate the structural change caused by simultaneous and sequential biaxial orientation, 2D-SAXS pattern of PP and PP nanocomposites before and after biaxial stretching is shown in Figure 4.6, where MD and TD stretch direction were indicated by arrows. The top row, from left to right, represents upstretched, simultaneous and sequential biaxially stretched neat PP, respectively. Similarly, the bottom row represents those of PPNC. Before stretching, two maxima along are shown along the meridian indicating the slightly oriented lamellar stacks in MD. This is due to the slight stretching during sheet extrusion process. There may coexist a small portion of unoriented lamellar or spherulites. Morphology with a coexisting small rows of lamellae and spherulites are suggested by Tabatabaei et al. [139] when cast roll set at a high temperature and polymer melt at the die exit was subjected to a high draw ratio. For simultaneous biaxial orientation, a circular pattern presents in both unfilled and filled films. This is a sign of the isotropous but in-plane oriented lamellae. After such a high area stretching ratio, the original oriented crystals and remaining spherulites are fragmented into smaller lamellae. These lamellas are oriented in MD-TD plane but also randomly distributed along the film plane. Unlike the observation in simultaneous biaxial orientation, an arcade pattern was observed with scattering maxima in sequential biaxially oriented films. This suggest a

preferential orientation instead of random distribution of lamellae.

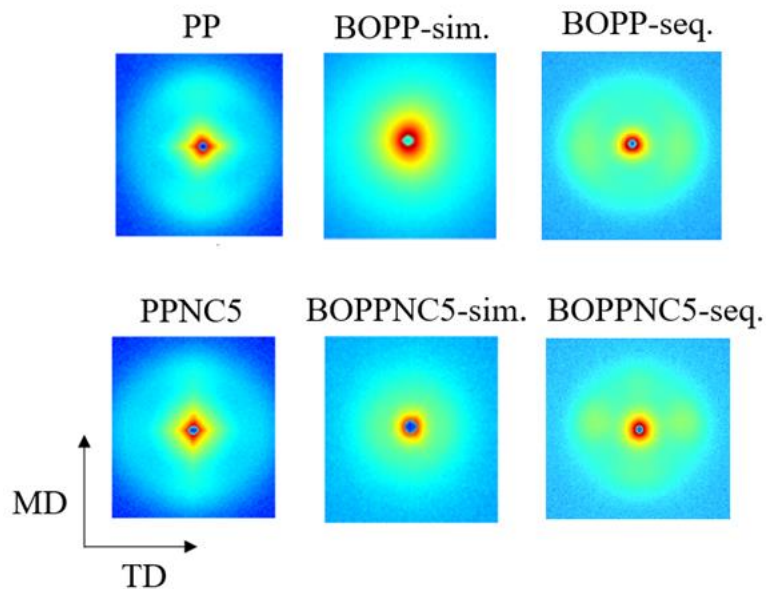


Figure 4.6 2D SAXS of extruded and biaxially stretched PP and PPNC.

The 2D SAXS analysis can also be correlated to the observation made by McIntyre and co-workers [140]. They used AFM to examine the surface morphology of sequentially biaxially oriented BOPP films and revealed a nanometer-scale fiber-like network structures. High TD and low MD stretching ratio resulted in a preferential arrangement of small fiber in the TD direction while some thicker veins present in parts of the network which were nominally oriented in the MD. For similar TD and MD ratio, there is no predominant fiber orientation and no larger veins. The latter could be considered close to simultaneously stretched BOPP in our case. Similar results were also reported where equi-simultaneous biaxial stretching results in the PP chains in both crystalline and amorphous regions to rotate towards the stretching direction, while sequential biaxial stretching, the molecular chains first oriented toward the MD in the first stretching, and then rotate to TD during the second stretching [36].

As for the influence of nanoclay, in general 2D SAXS patterns were similar in PPNC

compared to PP indicating a similar structure evolution but there is some difference. For simultaneous stretched samples, the contour of BOPP is slightly elliptic while that of BOPPNPC is more circular indicating a more isotropic distribution of lamellae in BOPPNPC. For sequentially stretched BOPP, two maxima were present predominately along equator suggesting preferential orientation of lamellae along second TD stretching direction while for sequentially stretched BOPPNPC, with incorporation of nanoclay, the maxima show in both equator and meridian, suggesting a preferential orientation of lamellae along both MD and TD., although the prevalence is still more remarkable in TD.

The 1D integrated SAXS intensity curves for simultaneously and sequentially stretched BOPP and BOPPNPC was summarized in Figure 4.7 (a), where x-axis represents the scattering vector q and y-axis is the Lorentz corrected intensity. A peak could be observed in the low q range in every sample which was attributed to the in-plane oriented lamellar stacks. Figure 4.7 (b) demonstrates the long period of lamellae of simultaneously and sequentially stretched BOPP and BOPPNPC, respectively. With regard to initial long period of $\sim 13\text{nm}$ in extruded PP and PPNC as shown in Chapter 3, clearly after biaxial orientation process, long period of lamellae in both PP and PPNC increases significantly. This can be correlated to the large strain-induced recrystallization and the extension of amorphous tie chains. The long period of final lamellae in sequentially stretched samples are larger than that in simultaneously stretched samples, although the total area stretching ratio is smaller in the former, which may suggest the final crystal dimension are more determined by the largest stretching ratio along an individual direction. In addition, under both stretching modes, long period of lamellae in final BOPPNPC is larger than BOPP. This could be associated with depressed equilibrium melting temperature and enhanced crystallization rate with presence of nanoclay.

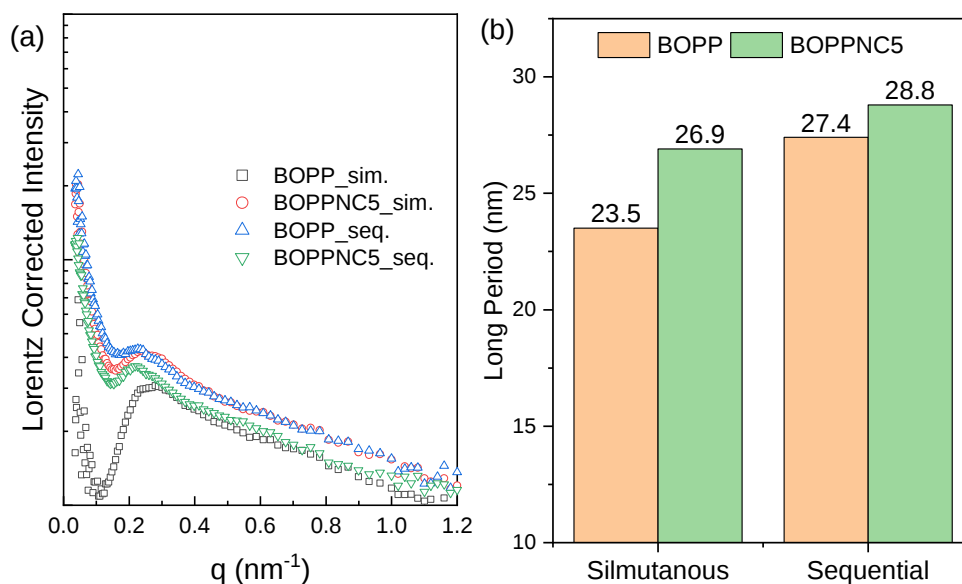


Figure 4.7 1D SAXS intensity profile and long period information of simultaneous and sequential biaxially stretched BOPP and BOPPNC. (a) 1D SAXS intensity profile; (b) Long period.

4.3.4 Mechanical property

Both simultaneously and sequentially biaxial stretched films were tensile tested along MD and TD in order to find the effect of stretching mode on the mechanical properties. Figure 4.8 (a) (b) (c) summarizes the tensile modulus, ultimate tensile strength, and elongation at break of different BOPP and BOPPNC films, respectively. First of all, biaxial stretching resulted in a significant enhancement of mechanical properties compared to unstretched PP. The tensile modulus rises to 3.31 / 3.15 GPa along MD / TD in simultaneously stretched BOPP and 2.79 / 3.44 GPa along MD / TD in sequentially stretched films. Apparently, the tensile modulus and ultimate tensile strength along MD were slightly higher than those along TD in simultaneously stretched films while in sequentially stretched films, the MD tensile modulus and ultimate strength was lower than TD. The addition of clay further increased the tensile modulus significantly (3.89 / 3.44 GPa along MD / TD in simultaneously stretched BOPPNC5 and 3.35 / 4.18 GPa along MD / TD in sequentially stretched BOPPNC5) when comparing

BOPP and BOPPNC under same stretching mode but did not change the trend between sequential and simultaneous stretching. Moreover, it seems that addition of nanoclay helps mitigate the difference between MD and TD especially in sequentially stretched films. Tensile strength results also follow similar trend between the two stretching modes. Combining Figure 4.1 and Figure 4.8, a correlation between the mechanical strength, the stretching ratio and force from the biaxial orientation could be established. Tensile properties were more enhanced along the direction with larger stretching ratio and higher stretching force. The high stretching force is associated with the higher degree of polymer chain orientation and clay nanofiller orientation during biaxial stretching which subsequently led to higher tensile modulus and strength. The slightly higher MD to TD mechanical strength in simultaneously stretched films is a result of pre-stretching in the precursor sheet while the larger difference between MD and TD property in sequentially stretched films is due to the inherent different stretching ratios. On the contrary, Figure 4.8 (c) shows that the elongation to break drops with increasing stretching ratio as expected. This is simply because that there is less potential for further stretching as the polymer chains has been oriented to a higher degree with increased stretching ratio. Addition of clay did not decrease the elongation at break. Moreover, in all cases, the elongation to break was still over 50% as a practical value for packaging film application.

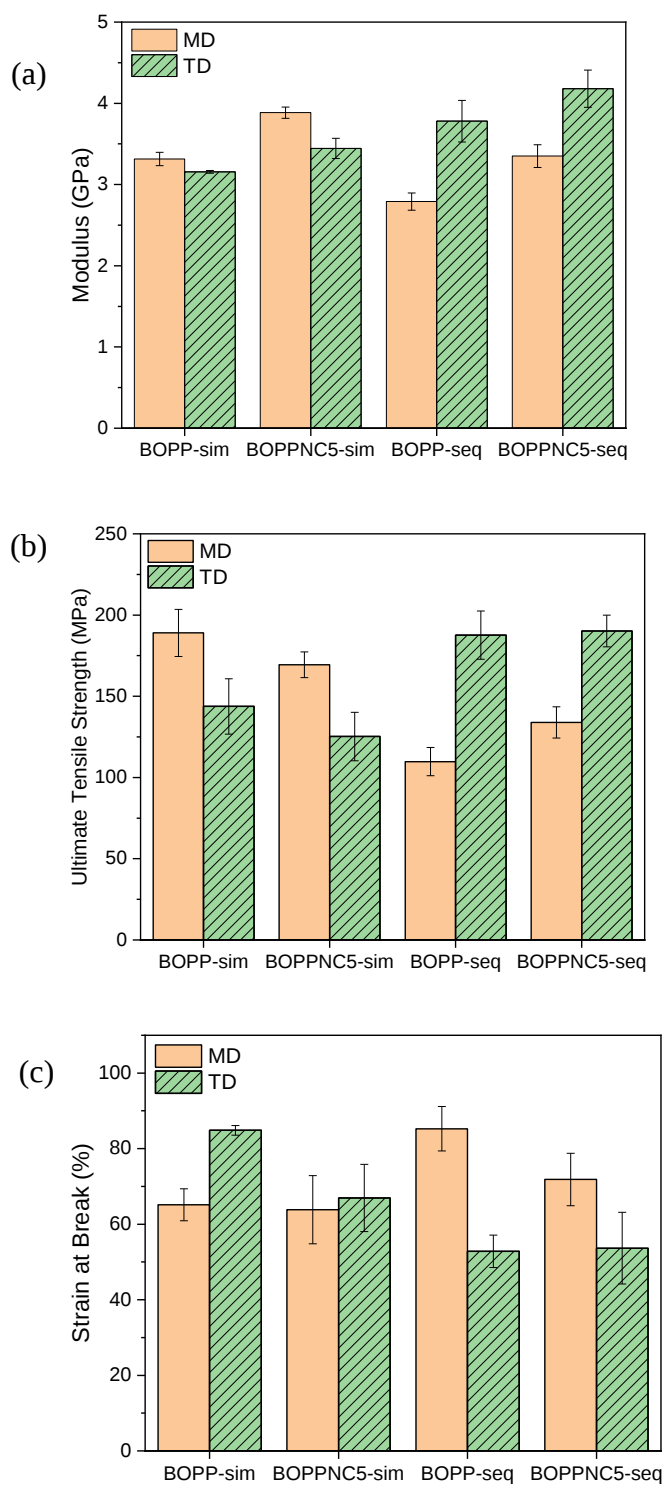


Figure 4.8 Tensile properties of simultaneously and sequentially stretched BOPP and BOPNC: (a) tensile modulus; (b) tensile strength; (c) elongation at break.

4.3.5 Barrier property

The results for oxygen permeability (OTR) of biaxially stretched films have been presented in Figure 4.9 with a calibrated sample thickness of 1 mil. Compared with extruded PP sheet with OTR of 3831 cc.mil/m².day as reported in last chapter, it is evident that both simultaneous and sequential biaxial stretching reduced oxygen permeability by at least 50%. This was attributed to increased crystallinity and crystalline orientation after a high stretching ratio. Furthermore, addition of 5wt% nanoclay further reduced oxygen permeability significantly in both simultaneously and sequentially stretched films by comparing BOPPNC5-sim to BOPP-sim and BOPPNC5-seq to BOPP-seq, respectively, indicating high degree of dispersion and orientation of clay nanolayers in both stretching modes. These clay nanolayers acts as impermeable obstacles by forcing the gas molecules diffused in a more tortuous pathway. Compared with sequentially stretched films, simultaneously stretched films exhibited a slightly higher oxygen barrier, which may be simply due to the fact that the area stretching ratio was slightly higher in simultaneous stretching compared to sequential stretching. The relatively lower stretching ratio of 5 along MD for sequential stretching may in all cases may also plays a role.

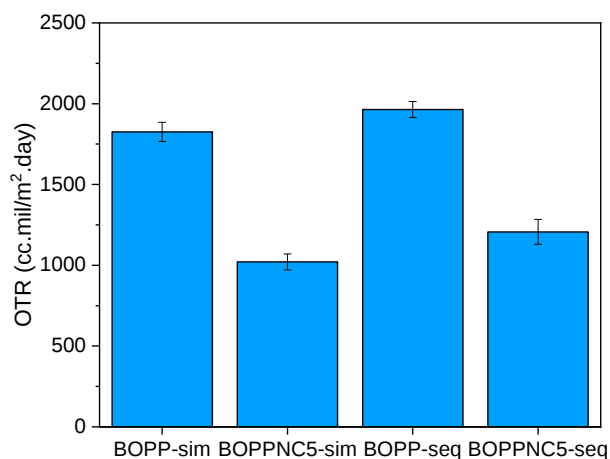


Figure 4.9 Oxygen permeability of simultaneously and equationally stretched BOPP and BOPPNC films.

4.4 Conclusions

In this work, the different characteristic biaxial deformation behavior of polypropylene clay nanocomposites when subject to simultaneous and sequential biaxial stretching was compared. Under selected processing conditions, it was found that during simultaneous biaxial stretching, the stress-strain curves of both PP and PPNC along MD and TD showed a typical ductile behavior with initial yielding followed by softening plateau and a strain hardening. During sequential stretching along MD, a less typical yield along with a much broader softening plateau and no strain hardening was observed. Along TD, absence of yielding point became more distinct with a rubbery trend and steadily increasing stress with increase strain. Moreover, there is a significant rise in overall stress levels for a given stretching ratio compared to that in simultaneous stretching. The effect of other processing parameters including stretching rate and temperature was also revealed. Strain rate affects the deformation behavior on a various scale depending on the stretching mode but the effect of stretching temperature is consistent and more dominant. 2D SAXS reveled the crystal structure development from extruded precursor to biaxially oriented films. Simultaneous stretching resulted in more isotropic orientation while

sequential stretching led to a preferential alignment of lamellae along two stretching direction especially TD. Sequential stretched nanocomposite films exhibited less balanced mechanic property compared to simultaneous stretched composite films but addition of nanoclay seem to abate such anisotropy. The barrier performance of simultaneous stretched films is slightly better than sequentially stretched films. These properties can be well related to the crystal structure in different films.

Chapter 5. Ultra-high expansion PP Nanocomposite Foam under supercritical CO₂: Rheology, Deformation, Structure, and Mechanical

5.1 Introduction

Polymer foams, with their cellular structure composed of gaseous voids surrounded by a denser continuous phase, have been widely used in construction, packaging, automobile, furniture and refrigeration industries due to their low density, insulation, cushioning and absorption abilities. Particularly, polymer foams represent a promising future for lightweight components to save materials and energy. Their unique structure and properties are determined by volume expansion ratio, cell density, cell size distribution, and cell structure (open or closed cell), which can be manipulated by the type of materials and foaming process techniques. Among diverse polymeric foams, polypropylene have attracted special interests due to their low cost, chemical stability, and high stiffness. More importantly, polypropylene possesses a higher melting temperature which guarantees a broader service temperature window. However, the most common isotactic linear polypropylene possesses two disadvantages towards foaming. On one hand, as a semi-crystalline polyolefin, the cellular structure is hard to control due to the fact that gases only dissolve in amorphous regions and do not dissolve in crystalline phase. This can lead to nonuniform microcellular structure as result of heterogeneous nucleation. On the other hand, linear PP exhibits relatively poor foam-ability due to the lack of required melt strength and melt elasticity which constrained its practical application [141–143]. The weak melt strength and the incapability to bear extensional force during bubble expansion led to a high risk of cell coalescence and foam rupture.

Considerable efforts have been dedicated to improve the foaming processability of linear PP. Blending with branched PP or expanded PP have been proven to be effective in

improving foamability of linear PP [144]. Branched PP induces higher melt strength and strain hardening that prevent bubble coalescence. However, the economic cost for production of branched PP is much higher compared to linear PP and the recyclability is be affected. Besides the blending technique, polymer nanocomposite foams incorporating nanofillers including clay [74,145,146], silica [147], CaCO_3 [148], nanofibers [149], has attracted significant interests for improving PP foamability. Of these nanofillers, clay, with a platelet-like layered structure, have been the most popular option offering high reinforcing efficiency at relative low loadings. It has been demonstrated that addition of nanoclay promotes various polymer foaming processes with a resultant more uniform cell size distribution. It allows a better control of foam microstructure and the properties. The increased melt strength and induced strain hardening in the low-melt-strength polymers were recognized as indispensable characteristics for polymer foaming as these endow polymer melts withstand high stretching force experienced during the latter stages of bubble growth [145,146]. Chaudhary and Jayaraman [74] correlated the observed improvements in fine foam microstructure with improved extensional strain hardening behaviour of PP nanocomposite melts. Münstedt et al. [150] also indicated that strain hardening is of advantage for the geometrical uniformity and processed items. The addition of nanoclay also enhances cell nucleation with increased cell density and optimal concentration was suggested [151]. Zheng et al. [152] also demonstrated the addition of nanoclay into linear PP lead to better cell morphology with both increased cell density and expansion ratio at an optimal temperature. Exfoliated nanocomposites can lead to more remarkable increase in cell density than intercalated nanocomposite [153]. They also indicated insufficient incorporation of clays is not able to suppress bubble coalescence while excessive loading would constrain cell growth. Other benefits of adding nanoclay includes reduced

escape of blowing agent from foam surface and more uniform foam skin with less roughness. Furthermore, an reinforcement in mechanical properties in polymer clay nanocomposite foams are reported as well as optimized cell structure and polymer matrix structure [154].

Recently, polymer foams with high expansion ratio are receiving increasing attention. On one hand, foams with low density meets the need to save material usage and energy consumption. On the other hand, foams with high expansion ratio exhibit better energy absorption, thermal and sound insulation [155]. To this end, the application of supercritical batch foaming in producing polymeric foams has attracted significant interests in recent years to produce foams with high cell densities and high expansion ratio. Supercritical gases have much higher solubility and diffusivity than their gas phase, leading to large dissolution in polymer matrix which in turn produces foam with expansion ratio significantly higher than that with chemical blowing agent. The formation of a saturated polymer-gas system are crucial to control the number of nucleation sites and cell size [156]. The process time is also shortened which favors industrial feasibility. Being environmentally-friendly, non-toxic, sustainable, and abundant, supercritical CO₂ has gained the most popularity among other physical blowing agents. The relative lower supercritical point of CO₂ (31.1°C, 73.8 Bar) is easier to achieve and thus saves energy. Consequently, a number of studies focused on understanding processing, structure and property in polymer foams from supercritical CO₂ batching foaming [157,158]. Li et al. [159] studied the temperature and pressure dependence of CO₂ diffusion in PPMA and the relationship between the saturation time and cell nucleation in batch foaming as it is crucial to control the number of nucleation sites and the critical cell size. Xu et al. [157] also investigated the effects of saturation time, foaming temperature, saturation pressure and depressurization rate on the foam structure and volume expansion ratio and indicated that

lower foaming temperature and a higher saturation pressure were more favorable for obtaining uniform foam. Doroudiani et al. [142] investigated the effect of crystalline morphology of semicrystalline polymers on the solubility and diffusivity of the blowing agent as well as the cellular structure of foams prepared via batch foaming. Zhong and co-workers [158] modified batch foaming method with supercritical CO₂ by reducing the crystalline effect via saturation with supercritical CO₂ at high temperature to disrupt crystalline regions. A dramatic depressurization initialized foam expansion with resultant small cells and high cell density. The foaming temperature range was also found 12 times broader than that compared to the conventional method. Furthermore, presence of supercritical CO₂ provides the plasticizing effect which allows melt foaming process at much lower temperatures while keeping polymer from crystallizing. The decreased operating temperature allows higher material stiffness to withstand bubble expansion to produce foams with high expansion.

Typical nanocomposite incorporating nanofillers for producing finer cell structure in foamed polypropylene or thermoplastic olefin blends (TPO) usually resulted in moderate expansion ratio. This may be overcome by the superficial batch foaming as described above. Furthermore, addition of silane treated organoclay nanoparticles also increase the foaming temperature window, which means less melting allowing a higher expansion potential. Therefore, foaming nanocomposite using supercritical batch foaming has the potential for ultra-high expansion ratio but still with good mechanical.

In this work, foamability of PP nanocomposites is evaluated with batch foaming using supercritical CO₂ in a pressure vessel. The nanocomposite foam cellular structure was compared with base PP foam. While the expansion ratio as well as the microcellular structure can be tuned with nanocomposite formulation, a remarkably high expansion ratio of 35.8 is

achieved in the nanocomposite. The nanoclay dispersion was analyzed compared to unfoamed samples. Extensional rheology and biaxial deformation behavior close to foaming conditions was investigated. The mechanical compressive properties of nanocomposite foam were also evaluated.

5.2 Materials and Characterization

5.2.1 Materials

The polypropylene grades used in this work was PP4792, supplied by ExxonMobil (MFI 2.7, ASTM 1238; density=0.90g/cm³), was used as in the supplemental work to investigate the effect of biaxial stretching temperature. The maleic anhydride-grafted PP (PPgMA) compatibilizer grade was Exxelor PO-1015 supplied by ExxonMobil, which is a random copolymer with ethylene (M_w = 123,000; 0.42wt% bound maleic anhydride). Organically modified montmorillonite Nanomer I.44P was obtained from Nanocor, which has a quaternary ammonium ion surfactant with two octadecyl tails. The reactive silane coupling agent was Dynasylan 1411, an aminoalkyl dimethoxysilane from Evonik.

5.2.2 Nanocomposite preparation

Silane treatment of nanoclay was conducted via a solvent-free process at Malvern Minerals Co. where the organoclay was exposed to a 0.8wt% refluxed silane vapor. This silane concentration was pre-determined as the optimized level for sufficient coupling. The treated organoclay was then sieved with a No. 200 mesh. Nanocomposites incorporating PP, PPgMA, and treated organoclay were compounded in a Leistritz twin screw extruder (diameter = 27 mm; L/D = 48) at 180 °C and RPM = 200. Before compounding, the PPgMA and grafted organoclay were dried in vacuum oven to remove moisture. A two-step compounding process involving a masterbatch and “let-down” was utilized. Two masterbatches were used, one

contained 1:1 clay: PPgMA concentration ratio and the other one contained 3:2 clay: PPgMA as well as comparable loading of base PP to improve the mixing. The “letdown” was then made by adding masterbatch to PP homopolymer to prepare nanocomposites with various clay loadings. The final composition of nanocomposites was presented in Table 1. Precursor sheets for biaxial orientation were prepared in a single screw sheet extrusion line.

Table 5.1 Compositions of PP/clay nanocomposites.

	Polymer matrix	Amount of clay (wt%)	PPgMA to clay ratio
PP-E	PP (MFI 2.0)	0	1:1
PPNC3-E	PP (MFI 2.0)	3	1:1
PPNC5-E	PP (MFI 2.0)	5	1:1
PPNC5B-E	PP (MFI 2.0)	5	2:3

5.2.3 Batch foaming

Disk samples of 2mm thickness prior to batch foaming were prepared via compression molding. Batch foaming is processed in non-stirred high-pressure vessel in stainless steel from Parr Instrument. A glass beaker was inserted to prevent contact between samples and vessel wall. A customized Teflon sheet was also inserted into the middle the beaker to help holding the sample in a free-standing fashion. Dry ice was the added as CO₂ source. The vessel was gradually heated to the preset temperature and pressure above supercritical point in a controlled manner. Once the temperature and pressure were achieved and then kept constant, the sample is immersed in supercritical CO₂ for predetermined time as 2 hours to obtain an equilibrium and saturated state. Foaming was triggered via a rapid depressurization by releasing the gas valve. Various saturation temperature and pressure were assessed. It should be mentioned that

depressurization rate was very fast and could be approximately calculated as the average of pressure drop divided by depressurization time. During the gas releasing process, it was always faster in the beginning and slower later. Nevertheless, the average depressurization rate was considered as a reasonable assessment for comparative purpose. The reaction vessel was transferred into cooling water bath immediately after gas releasing to stabilize the foam structure.

5.2.4 Characterization

The volume expansion ratio of the obtained foam, was defined as the ratio of density of unfoamed bulk materials to that of the foamed ones:

$$R_v = \frac{\rho_0}{\rho_f} \quad (5.1)$$

Where ρ_0 is the bulk density of unfoamed virgin material, ρ_f is the density of foamed material. The density of unfoamed and foamed samples is measured using a water displacement method via Sartorius YDK01 density measurement kit following ASTM D792 based on Archimedes' principle. The buoyancy force equals to the mass of the volume of the liquid displaced by the sample. To compensate for the sinking effect, the density the foam is calculated as follows:

$$\rho_f = \frac{w_a * \rho_l}{(w_a - w_l)} \quad (5.2)$$

Where is the density of the foam sample, w_a is the mass of sample in air, w_l is the mass of the sample when completely immersed in water, ρ_l is the density of water.

The cellular structure of the foams was observed by JEOL-6610LV scanning electron microscope. The samples were cryogenically fractured after immersed in liquid nitrogen for 30 mins. The fracture cross-section is sputter coated with gold. SEM observation is conducted using an accelerating voltage of 12KV and spot size of 30mm. The micrographs were analyzed

using Image J software. The cell size is determined as the number average diameters of all cells in the image. Cell size distribution is also statistically analyzed. The cell density is determined as the number of cells per unit volume of the foam, which was calculated using Eq. 5.3:

$$N = \left(\frac{n}{A}\right)^{\frac{3}{2}} * R_v \quad (5.3)$$

Where n is the total number of cells in the micrograph, A is the image area, R_v is the expansion ratio.

Transmission electron microscope (TEM) was carried out on a JEOL 100CXII transmission electron microscope to investigate and assess clay dispersion in both unfoamed and foamed nanocomposite. Images were obtained operated at a voltage of 80kv. A 90nm-thin slice of biaxially oriented film was prepared by microtoming along the cross-section of the sample and collected onto a 300-mesh copper grid.

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 8 tons for 10 min at 200°C. The extensional viscosity measurements were performed at 180°C and two Hencky strain rates 0.1 s⁻¹, and 1 s⁻¹ up to a Hencky strain of 3.

Equi-simultaneous biaxially stretching of PP and PP nanocomposite samples was carried out on a Karo IV biaxial apparatus at Brückner, Siegsdorf, Germany. Square specimen (90 mm × 90 mm) was cut from the melt-extruded precursor sheets. The annealing oven as well as the stretching oven were held at same heated temperature, which was selected at 150°C and 155°C close to the foaming temperature range. After preheating, the samples were biaxially stretched under a range of processing conditions. Two strain rate of 100% s⁻¹ and 50

%⁻¹ were applied which was considered to resemble that at later stage of expansion. Forces and displacements were recorded during the stretching process and stress-strain curves were generated based on these data. All the samples are stretched until breakage to probe the stretching possibility.

The quasi-static mechanical compressive behavior of PP and PP nanocomposite foams was characterized in uniaxial compression carried out on a universal testing machine, Instron 5982, at room temperature under quasi-static conditions, employing a displacement rate of 0.01 s⁻¹ depending on the sample geometry. The foams were compressed to a maximum strain of 90 %. Compression force loaded and crosshead displacement were measured and recorded by the Instron machine. The compression force load and crosshead displacement were measured and recorded by the Instron machine. The nominal stress was calculated as:

$$\sigma = \frac{F}{A} \quad (5.1)$$

where F was the force applied by the Instron machine and A was the cross-sectional area of the sample. The nominal strain was calculated as:

$$\varepsilon = \frac{\delta}{h} \quad (5.2)$$

where δ was the crosshead displacement of the Instron machine and h was the thickness of test specimen.

5.3 Results and discussion

5.3.1 Foam expansion

The unfoamed disk and expanded PP and PP nanocomposite foam samples are presented in Figure 5.1 and Table 5.1 presented the corresponding expansion ratios for each sample. It should be mentioned the PP was foamed 150°C while all the PP nanocomposites

shown was foamed at 153°C. This is considered due to the fact at, the relative weak melt strength of base PP could not hold the freestanding condition in the saturation stage during experimental setup. While the PP foam exhibited a low expansion ratio with only 2.1, the expansion ratio in all nanocomposites showed a significant increase, from 13.1 in PPNC3-E to an unprecedented 35.8 in PPNC5B-E foam. It is apparent that by increasing the nanoclay loading from 3wt% to 5wt% and further optimize the PPgMA compatible content, the expansion ratio can be tuned at the same foaming condition. This result thus illustrates the flexibility of PP nanocomposite foaming for manipulated foamability.

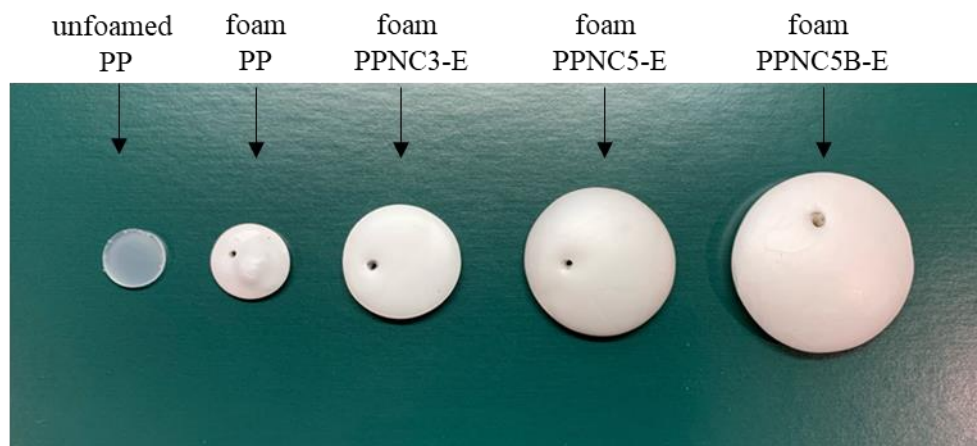


Figure 5.1 Unfoamed disk and expanded pp and pp nanocomposite foam.

Table 5.1 Expansion ratio, average cell size and cell density of PP and nanocomposite foam.

	PP-E*	PPNC3-E	PPNC5-E	PPNC5B-E
Expansion ratio	2.1	13.1	28.0	35.8
Average cell size/μm	9.3	18.9	63.1	105.9
Cell density number/cm^3	6.5×10^6	1.9×10^8	2.1×10^7	1.5×10^7

*PP was foamed at 150°C, 180bar; all nanocomposite was foamed at 153°C, 160bar

5.3.2 Cellular structure

Figure 5.2 SEM micrographs of PP and nanocomposite foam (a) PP-E foam; (b) PPNC3-E foam; (c) PPNC5-E foam; (d) PPNC5B-E foam. shows the typical results of SEM images of the fracture surfaces of PP and PP nanocomposite foam. The cellular microstructure was quite different between PP and nanocomposite. While the base PP foam, with its very low expansion ratio, exhibited spherical closed-cell structures, the nanocomposite foams exhibited well-defined polygon closed-cell structures with pentagonal and hexagonal faces especially in PPNC5-E and PPNC5B-E foam, which has been considered as the most energetically stable form. The average cell size was statistically measured and summarized in Table 5.1. It is clear that the cell size increases with increasing expansion ratio from PP to PP nanocomposite foams. The cell size distribution was also presented in Figure 5.3. Due to the huge difference between cell size, in each case, the statistics of cell size distribution used respective bins and scale. Based on the SEM images and cell size distribution, it can be concluded that PPNC5-E and PPNC5B-E foam exhibited uniform cell size distribution especially in PPNC5B-E foam with a dominant peak around 100 μm .

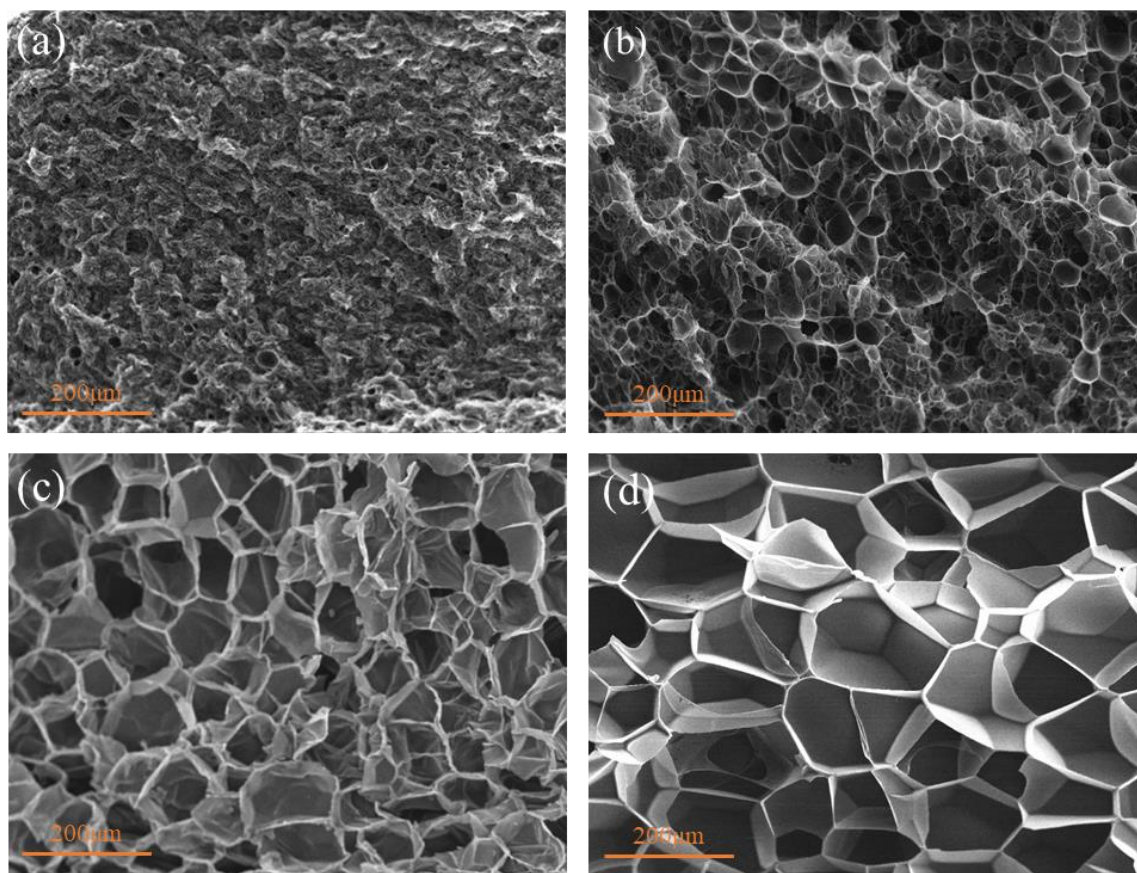


Figure 5.2 SEM micrographs of PP and nanocomposite foam (a) PP-E foam; (b) PPNC3-E foam; (c) PPNC5-E foam; (d) PPNC5B-E foam.

The cell density was calculated and shown in Table 5.1 as well. The cell density in nanocomposite foam was considerable higher than that in the neat PP foams, this suggests that that the dispersed clay nanolayers act nucleating sites for cell formation. It is considered well-dispersed nanoclay reduces the energy barrier of cell nucleation by inducing a local stress variation in polymer/gas solutions[151].

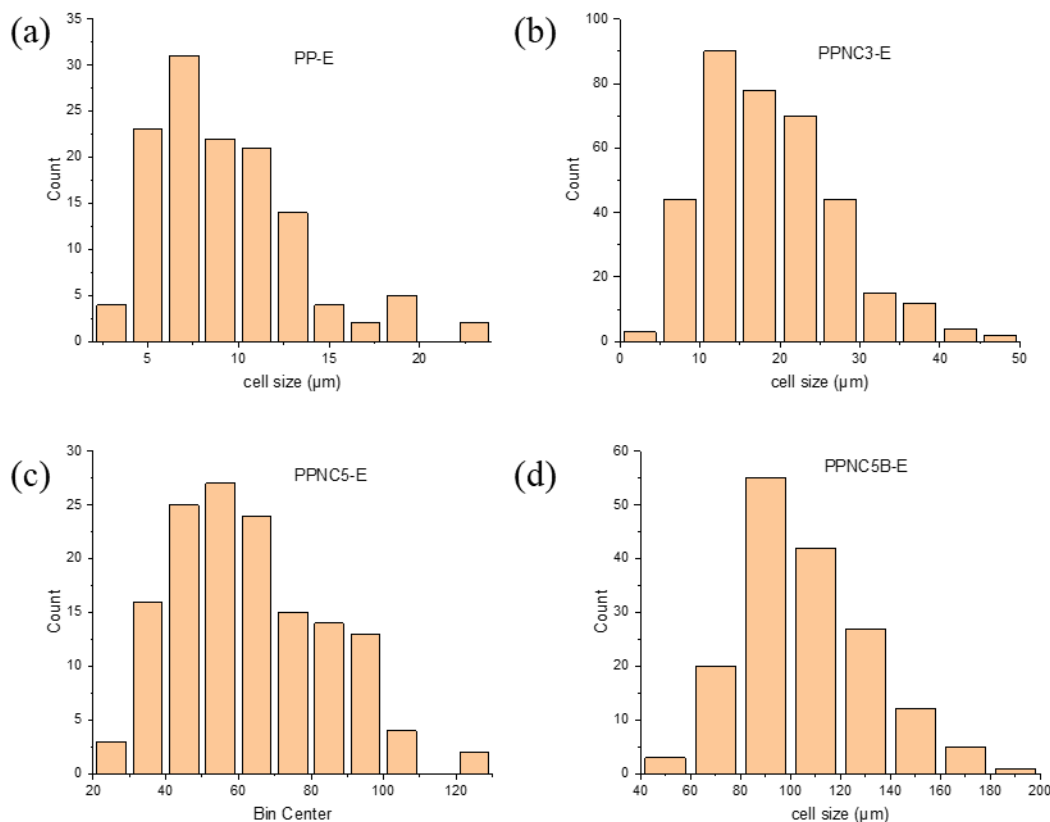


Figure 5.3 Cell size distribution of PP and PP nanocomposite foam (a) PP-E foam; (b) PPNC3-E foam; (c) PPNC5-E foam; (d) PPNC5B-E foam.

5.3.3 Clay dispersion

TEM micrographs of the unfoamed and foamed nanocomposites with organically modified nanoclay are shown in Figure 5.4. In TEM micrographs, the clay nanoparticles appear as dark black spots or lines while the background represents the matrix phase including PP and PPgMA compatibilizer. In the unfoamed nanocomposite as shown in Figure 5.4 (b) (c) shows the clay dispersion in the foamed nanocomposite. Although there is some difficulty in the obtaining a “flat” microtome foamed sample due to the complex cellular structure and cell stacking as shown in Figure, where b is an example of a debris of cell well and c is another location of the same sample, we still managed to achieve good observation in limited good samples shown in Figure 5.4 (d) (e), which showed a debris of the cell wall with its edges

shown under lower and higher magnification, respectively. Clearly, the TEM image from the foamed nanocomposite exhibited enhanced alignment of clay nanolayers induced by the expansion deformation in cell growth stage. Compared to unfoamed nanocomposite, an increased delamination with partial exfoliation was also observed. These orientation and exfoliation of the clay particles may help thin cell walls to withstand the extensional force from breakage. A similar result was also reported by Okamoto et al. [145] and they identified the biaxial flow-induced alignment of clay particles along the cell boundary. They also observed a random dispersion of clay in the junction region between three contacting cell which was considered to be affected by the stagnation flow between adjacent cell walls during cell growth.

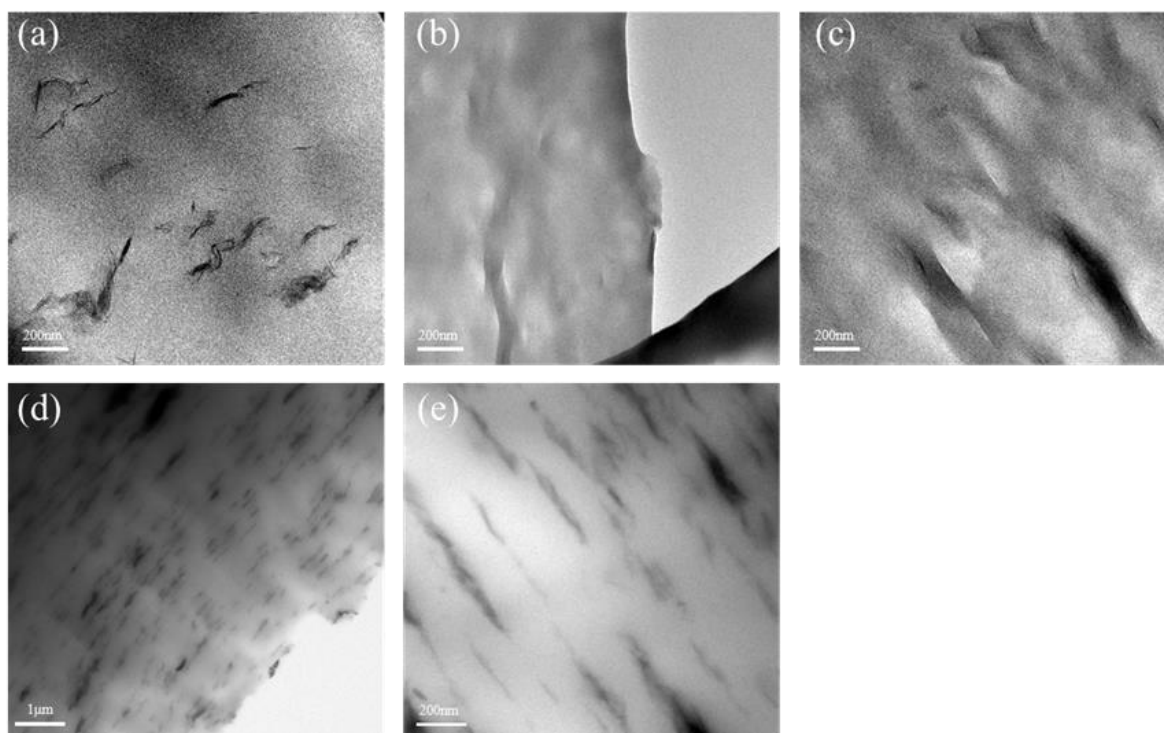


Figure 5.4 Representative TEM micrographs for unformed and foamed PP nanocomposite (a) unfoamed, compression molded PPNC5B; (b) foamed PPNC5B close to a cell edge, “poor” sample; (c) foamed PPNC5B in cell middle, “poor” sample; (d) foamed PPNC5B close to a cell edge at low magnification, good sample ; (e) foamed PPNC5B at higher magnification, good sample.

5.3.4 Extensional rheology

Although the foam processing in this study was conducted at the temperature slightly below melting temperature, due to the supercritical CO₂ dissolved which can act as a plasticizer, the melt rheological behavior especially the strain hardening is essential. Li and co-workers [160] actually investigate the relation between the crystallization and foaming of PP via an in-situ visualization and confirmed the CO₂ dissolved in polymer melt depresses the crystallization temperature and nucleation of PP. Specifically, the onset of melting temperature drops by approximately 1.08 °C for every 1 MPa in the range of 0 -15 MPa. The uniaxial melt extensional viscosity transients at strain rates ranging from 0.1 s⁻¹ to 1 s⁻¹ at 180 °C of PP and PP nanocomposites have been presented in Figure 5.5 Uniaxial melt extensional viscosity transients (η^e) at several strain rates for PP and PP nanocomposites. A maximum Hencky strain of 3 was set as the limit in each run. Strain hardening of the melt is defined as an upward deviation of the extensional viscosity from the linear viscoelastic envelope and it has been recognized as an indispensable characteristic to prevent cell coalescence and lead to higher cell concentrations [161]. As shown in Figure 5.5, the transient extensional viscosity data for base PP did not display any strain hardening. On the other hand, all the nanocomposites exhibited a strain hardening behavior, and that trend is more significant at higher strain rate. This is ascribed to both the clay nanolayers and the high molecular weight PPgMA compatibilizer. The extent of strain hardening, or a strain hardening ratio χ , was quantified as the ratio between transient extensional viscosity at given strain and in linear extensional viscosity regime. The value of calculated extensional viscosity based on the base line. The base line or linear viscoelastic “envelope” was obtained extrapolating the linear viscoelastic portion of each curves, typically between the data from strain of 0.1 to 0.4. The maximum strain

hardening ratio at each strain rate was evaluated at the highest viscosity level before the stretched specimen beaks or a necking occurs. Table 5.2 Maximum strain hardening ratio for polymer melt at 180 listed all the maximum strain hardening ratios and PPNC5B-E displays the highest value compared to other two nanocomposites, which corresponds to the highest expansion ratio achieved in the batch foaming process. In addition, although in Figure 5.5 the nanocomposite curves have been shifted, before shifting the viscosity level in all nanocomposites is higher than that in base PP indicating the enhanced melt strength which also plays an important role in promoting the foaming stability.

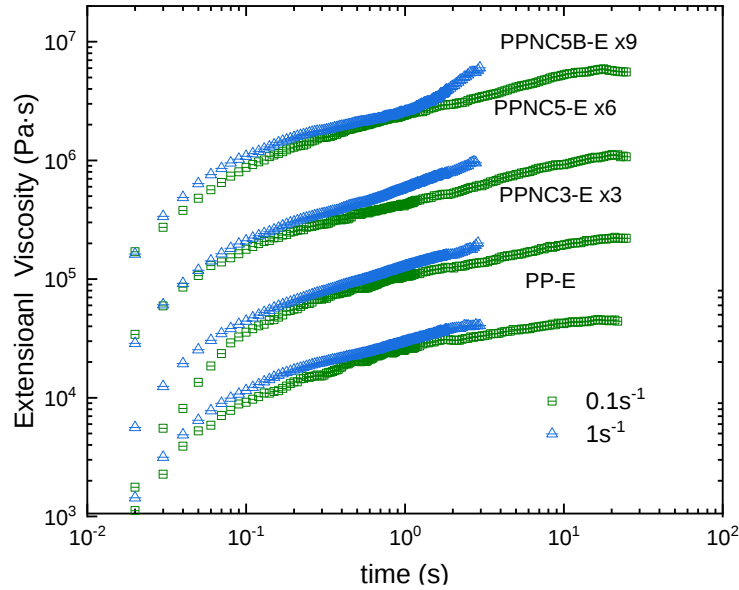


Figure 5.5 Uniaxial melt extensional viscosity transients (η^e) at several strain rates for PP and PP nanocomposites.

Table 5.2 Maximum strain hardening ratio for polymer melt at 180 °C.

Strain rate (s ⁻¹)	Strain hardening parameter			
	PP-E*	PPNC3-E	PPNC5-E	PPNC5B-E
0.1	NA	1.40	1.56	1.77
1	NA	1.23	1.17	1.35

5.3.5 *Biaxial deformation behavior*

While extensional viscosity rheology measures the deformation behavior of polymer melts under a uniaxial tension, the actual gas expansion when foaming polymers is considered to create a biaxial tension such as encountered in thermoforming process although some researchers suggest if strain hardening is observed in uniaxial extensional flow, it is expected to occur in biaxial extensional flow as well [150]. Furthermore, despite that foaming was generally considered primarily occurs during melt state, at the selected condition in this research, the foam expansion may also occur during both melt and semi-solid state before complete crystallization finalizing the foam structure. Therefore, it is essential to study the material response subjected to biaxial deformation tension as well. The equi-simultaneous biaxial stretching deformation behavior of the materials used in this research was investigated a biaxial test rig at temperature similar to the foaming temperature. All the materials are biaxially drawn until breakage.

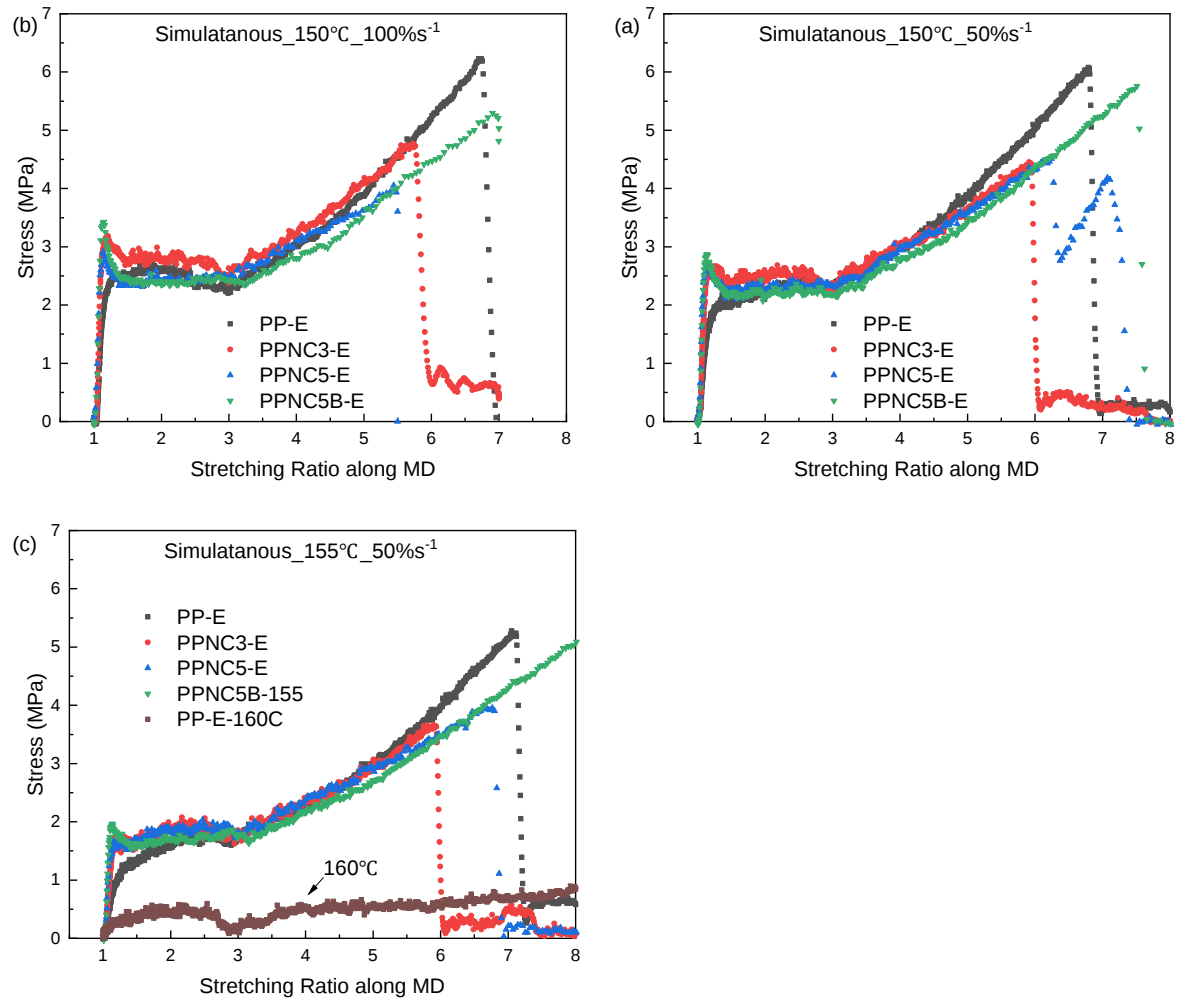


Figure 5.6 Biaxial deformation behavior of PP and PP nanocomposites at different stretch temperature and strain rates (a) 150 °C and 50%⁻¹; (b) 150 °C and 100%⁻¹; (c) 155 °C and 50%⁻¹, deformation behavior neat PP 160 °C 50%⁻¹ of is inserted with arrow.

Figure 5.6 (a) (b) (c) showed the stress-strain response of PP and PP nanocomposites at stretch temperature and strain rate of 150 °C and 50%⁻¹, 150 °C and 100%⁻¹, 155 °C and 50%⁻¹, respectively. The effect of temperature and strain rate on the deformation behavior during simultaneous biaxial stretching has been discussed in previous chapter. Under all three conditions, both PP and PP nanocomposite can be stretched to relative high strain ratio at this semi-solid state. Addition of nanoclay resulted in a more ductile behavior in nanocomposites with increased modulus, higher yielding stress as well as a more distinct yielding behavior. At

high strain, there is a crossover of the biaxial stress-strain response observed at high strain between the nanocomposite and the base PP. This is suspected to relate to the further delamination of clay nanolayer which may act as an energy dissipation mechanism leading to a reduced stress may actually help with the relative high expansion ratio and large cell size obtained, but the essential strain hardening characteristic is still reserved for foaming stability. This relative low stress level may actually benefit relative high expansion ratio with larger cell size obtained. In conclude, the biaxial deformation behavior of all the nanocomposite could be connected to their foamability. The elongation at break, i.e., the maximum area stretching ratio of PP and PP nanocomposite has been summarized in Figure 5.7. Surprisingly, the PPNC5B-E actually achieved the highest stretching ratios in all selected test conditions. This is consistent with the highest expansion ratio achieved in PPNC5B-E compared to other materials. All these observations indicated the optimal PPgMA to clay ratio in PPNC5B-E to promote nanoclay dispersion and stretchability compared to other nanocomposites.

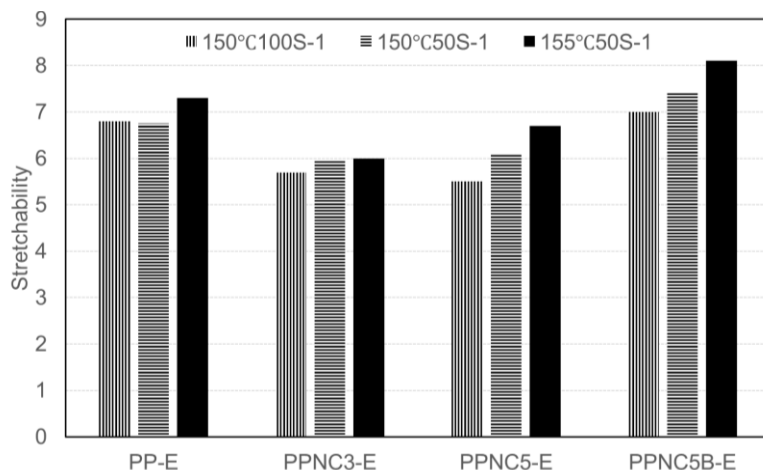


Figure 5.7 Maximum stretching ratio along one direction of PP and PP nanocomposite when subject to biaxial deformation.

In addition, the biaxial deformation behavior of base PP at 160 °C and 50%⁻¹ was

inserted in Figure 5.6 (c). At this temperature, PP is close to complete total melt as the stress level is tremendously lower than that at 155 °C and 50%⁻¹. There is no strain hardening behavior shown. This may explain the fact that PP cannot be foamed at the same condition as nanocomposite. To conclude, it is anticipated that the melt strength, the melt strain hardening behavior as well as higher modulus at early stage of semi-solid biaxial deformation helps prevent cell coalescence ; the stress level at later stage of semi-solid biaxial deformation allows higher expansion potential before total crystallization which lead to a high expansion ratio. In particular, the biaxial deformation behavior of all the nanocomposite shows more connection with their foamability.

5.3.6 Compressive behavior of foams

The compressive stress–strain behaviors of PP and PP nanocomposite foams under quasi-static compression (strain rate equals about 0.01s⁻¹) are shown in Figure 5.8 Quasi-static compressive stress–strain curves of EPP foams at about approximately 1 s⁻¹ (a) loading (b) loading-unloading. The stress-strain was only plotted below a fixed stress value near 90% of sample thickness for better comparison. As for PP foam, an elastic behavior is present at beginning of compression, i.e., low strain, this is simply a consequence of the fac that lowest expanded PP foam has a large portion of bulk materials which shows the elasticity upon initial compression. For nanocomposite foams, only PPNC3-E foam showed the initial elasticity while it is insignificant in PPNC5-E and PPNC5B-E due to the large pore volume fraction. Compared to PP foam, the nanocomposite foams exhibited high compressibility as a dramatic volume change with slightly increasing pressure, forming a stress plateau in the curve. The cells collapse by elastic or plastic buckling during the stress plateau phase. where a significant amount of specific energy can be absorbed [162]. The width of the plateau is determined by

the pore volume of foams [163], which is inversely proportional to expansion ratio. Consequently, PP foam shows almost no plateau while in the nanocomposite the plateau width increased gradually from PPN3-E to PPNC5B-E which is consistent with the expansion results summarized in Figure 5.1. Although there is almost no plateau shown in PP foam, there is a change in the slope of curve which corresponds to the beginning of cell collapse. With comparison of stress-strain curves in all samples, it seems that the plateau stress level as well the onset of collapse stress is solely dependent on the expansion ratio of the foam regardless of the material. These stress values increase with decreased expansion ratio, that is, increase foam density. One slight exception is the comparison between PPNC5-E and PPNC5, where the former shows similar onset of collapse stress which is probably due to reduced usage of relatively weaker PPgMA compatibilizer. Figure 5.8 represents the loading-unloading behaviour of the nanocomposite. As the compression force is removed, the pressure drops quickly. The area within the curve indicates the mechanical energy that can be absorbed.

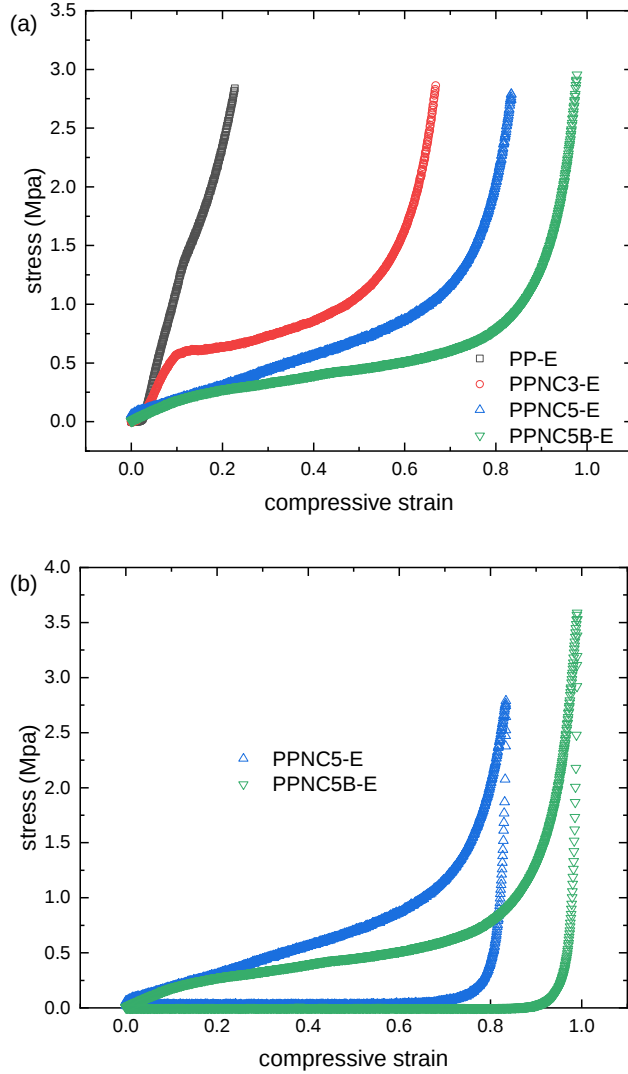


Figure 5.8 Quasi-static compressive stress–strain curves of EPP foams at about approximately 1 s^{-1} (a) loading (b) loading-unloading.

It is expected that the implementation of clay nanolayers can lead to a reinforcement in the mechanical of foams, by strengthening the cell walls. The clay particles may act as a secondary cloth layer to protect the cell with so thin cell walls from being destroyed by external forces [145]. However, there is a lack of samples under controlled comparison in our current experiment. The reinforcement effect can only be verified between PP and PP foams with same expansion ratio. In addition, Lataillade and co-workers [164] has indicated that although larger

cells (longer and thicker cell walls) are more prone to bend or buckle during quasi-static loadings, but under dynamic loadings they tend to be stronger due to the micro-inertia effect which makes them more difficult to bend or buckle. Therefore, a further investigation is focused on dynamic compressive behavior in these nanofoams.

5.4 Conclusions

Novel polypropylene nanocomposites were prepared in this work and evaluated with batch foaming using supercritical CO₂ in a pressure vessel. The high melt strength and addition of nanoclay helps the nanocomposite foam cell withstand the high expansion force. Nanoclay also increased the cell density significantly. Combining both factors, the nanocomposite foam exhibited an ultra-high expansion ratio up to 35.8 as well as a fine cell structure compared to base PP foam. The dispersion and alignment of nanolayer in foamed nanocomposite was also compared to unfoamed samples and it was found the foam expansion led to enhanced delamination and orientation of clay nanolayers. Strain hardening behavior is also confirmed in the nanocomposite via extensional rheology. Biaxial stretching at elevated temperature close to batch foaming temperature also showed the high stretchability of PP nanocomposites where the maximum area stretching ratio can be correlated to the maximum expansion ratio. Mechanical compressive test demonstrated that high compressibility as well as strength were maintained in the nanocomposite foam. These results demonstrated the possibility to achieve high expansion ratios in TPO composites consisting ternary systems of a crystalline PP matrix, a dispersed elastomer, and a filler in a next-phase study.

Chapter 6. Additives and Blends for Translucent Thermoplastic Polyolefin (TPO) Automotive Bumper Fascia

6.1 Introduction

Thermoplastic polyolefin (TPO) has been widely used in automotive industry for both exterior components such as bumper fascia and interior materials such as dashboard and door panel. It is essentially a polymer blends composed of continuous polyolefin phase such as semi-crystalline PP and dispersed elastomer phase such as ethylene propylene diene terpolymer (EPDM), ethylene-co-octene (EOC), ethylene-propylene (EP) rubber or styrene-butadiene-styrene triblock copolymer (SEBS), etc. TPOs retain the advantage of PP including stiffness, lightweight, ease of processing, and chemical resistance while the addition of rubber phase toughened PP with better ductility and impact resistance. Yet, the dispersed rubber phase would dramatically reduce the rigidity of PP matrix. Rigid filler such as talc has been commonly added into TPO which can greatly reinforce the strength and modulus of PP because of its rigid nature [165]. In fact, TPOs are compounded with a significant amount of talc to provide a tailored balance between stiffness and impact resistance, as well as better thermal stability depending on the end-use application.

With the growing automotive market especially the rapid growth in the segment of hybrid electric vehicles (HEV) or electric vehicles (EV) which integrates more display or lighting techniques, there is a potential market for translucent TPO for protection purpose. For example, BMW recently exhibited a color changing concept car based on their EV model ix at 2022 Consumer Electronics Show (CES). However, achieving relatively good clarity in TPO is constrained. This is due to density difference where the amorphous rubber particles dispersed in crystalline PP matrix can act a light scattering obstacle especially when the

particle size are large enough. Moreover, the commonly used talc is larger particle which may cause more severe light scattering effect.

One strategy to alleviate this dilemma is constructing nanocomposite by incorporating nanoparticles. Compared to tradition filler such as talc, addition of nanoparticles provides remarkable reinforcement effect at a low loading due to their large surface area. The dimension of these nanoparticles can be smaller than the visible-light wavelength thus alleviating the effect of scattering. There has been a number of studies focused on TPO nanocomposite incorporating nanoparticle such as nanoclay or nano calcium carbonate CaCO_3 , but most put emphasis on the mechanical performance [166–170]. It has been shown that the flexural modulus increases with increasing nanoparticle content but the effect on impact strength is not consistent. Lee et al. [171] indicated that the different effect on impact strength may also dependent on the concentration of elastomer phase. The number of research focused on optical properties are limited. Soulestin at al. [172] compared clarity, gloss, haze for clay added polyamide composites with different dispersion state and they found the optical properties are worse for the micro composites and better for the nanocomposites. Furthermore, addition of nanoparticles into TPO may lead to a decrease in elastomer particle size, which has been reported in a number of studies. This is most likely due to the effect of nanoparticle increasing melt viscosity and preventing elastomer phase coalescence [171]. The reduced elastomer particle size is expected to cause a significant decrease in light scattering. However, the elastomer particle size has to retain a reasonable value for toughening effect. Therefore an optimal concentration of particle fillers and optimal elastomer phase size are required. On the other hand, combination of two nanofillers can be feasible. Leong et al. [173] investigated the mechanical and thermal properties of polypropylene hybrid composites incorporating both of

talc and calcium carbonate. They have found a successful synergistic effect with both the flexural strength and impact strength being the highest among the hybrids when the PP/talc/CaCO₃ weight ratio was 70:15:15.

The other strategy to build a translucent thermoplastic polyolefin is via incorporating a clarifying polymer additive such as external elastomer. Bernreitner and co-workers [174] proposed a possible solution for achieving both low temperature impact strength and clarity. By blending two different types of elastomer, such as an external SEBS to EOC phase, they were able to achieve good balance between optical and mechanical properties. The combination of density matching and compatibilizer effect were considered to play a role. They also indicated that in any case modification based on a multi-phase blends deliver better performance. Similar, Yang et al. [175] found that SEBS could be used to modify homo polypropylene and random co-propylene with good impact properties as well as improve clarity.

In the present work, we intend to verify the effectiveness of the two strategies in an effort to obtain translucent TPO without sacrificing mechanical strength. Various polymer blends with various nanofillers and elastomer additive were evaluated in terms of optical and mechanical properties. A first effort was to modify a commercial grade TPO incorporating nanofillers and rubber blends. Then, a second step involves an effort for designing polymer blends composition to construct customized TPO with or without nanoparticle additives. Since this is an ongoing project, morphology of some samples was examined here. The optical property, flexural modulus and impact strength was compared.

6.2 Materials and Characterization

6.2.1 Materials

One commercial grade TPO (TPO-1) was used in this research as a reference material: Hifax 7430P (MFI 18.0, ASTM 1238; density=0.91 g/cm³), supplied by LyondellBasell, a UV-stabilized, paintable, unfilled thermoplastic elastomeric olefin (TEO) typically used for automotive exterior. Three polypropylene grades were used in this work: PP526P (MFI 8.0, ASTM 1238; density=0.90 g/cm³), supplied by Sabic, a homopolymer specially developed for cast film application; PP1105E1 (MFI 35, ASTM 1238; density=0.90g/cm³), supplied by ExxonMobil, a high melt flow rate homopolymer designed for general purpose injection molding; PP3485WZ (MFI 4.1, ASTM 1238; density=0.90g/cm³), supplied by Total Energies, a nucleated homopolymer designed for thermoforming. Three elastomer were used: a hydronated styrene-butadiene-styrene triblock copolymer, SEBS G1657 (MFI 22, ASTM 1238; density=0.90g/cm³), supplied from Kraton, which has a styrene to rubber ratio of 13/87 wt.% and consists of 65% triblock and 35% deblock.

The maleic anhydride-grafted PP (PPgMA) compatibilizer grade was Exxelor PO-1015 supplied by ExxonMobil, which is a random copolymer with ethylene ($M_w = 123,000$; 0.42wt% bound maleic anhydride). Calcium carbonate (CaCO₃) nanoparticles was obtained from SkySpring Nanomaterials, Inc. The average particle diameter was 15-40 nm. The surface was modified for enhanced interfacial interaction with PP/PE and improved dispersion. Organically modified montmorillonite Nanomer I.44P was obtained from Nanocor, which has a quaternary onium ion surfactant with two octadecyl tails and modified with silane coupling agent, Dynasylan 1411, an aminoalkyl dimethoxysilane from Evonik.

6.2.2 Blends and nanocomposite preparation

All the blends and nanocomposites were compounded via a Leistritz twin screw extruder (diameter = 27 mm; L/D = 48) at 200°C and RPM = 200. Either a one-step process with direct compounding or a two-step compounding process involving a masterbatch and “let-down” was utilized. The final composition of nanocomposites will be presented in later section. Pellets of blends or nanocomposite were dried at 80°C for at least 2h in a vacuum oven followed by being injection molded to various testing specimens including round disk, rectangular bars and dog-bone bars via a DSM mini injection molder under 200 °C and 60 psi.

6.2.3 Characterization

Optical measurements were conducted with a Rhopoint ID-T imaging transmission appearance meter which utilizes imaging-based analysis. The samples were placed atop the graticule, either in direct contact or at a predetermined spacer. Transmittance and haze value were obtained after image acquisition and data processing using the instrument's built-in software. Five measurements were conducted, and the average value was reported.

The cross section of biaxially oriented nanocomposite film is observed by JEOL-6610LV scanning electron microscope. The samples were cryogenically fractured after immersed in liquid nitrogen for 30 mins. The fractured cross-section is sputter coated with gold. SEM observation is conducted using an accelerating voltage of 12KV and spot size of 30mm.

Flexural modulus tests were conducted with a United Testing Systems (UTS) model SFM-20 according to ASTM-D790. Notched Izod impact tests were conducted with an TMI impact testing machine at ambient temperature according to ASTM-D256 with a standardized pendulum-type hammer. The test specimens were notched and conditioned at least 24 hrs.

before testing. At least three samples were tested, and mean values were reported.

6.3 Results and Discussion

6.3.1 Effect of nano CaCO_3 on TPO1

The commercial grade TPO1 has been modified with various amount of CaCO_3 nanoparticles. Table 6.1 summarized the corresponding composition, optical performance and mechanical properties including flexural modulus and impact test. There is an optimal of 5wt% CaCO_3 as indicated from the optical measurements. On the contrary, adding 10 wt% CaCO_3 into pure PP matrix shows a detrimental effect on the optical performance as comparing PP-S and PP-S-N1.

Table 6.1 Effect of CaCO_3 and SEBS on optical performance of TPO1.

	TPO1	CaCO_3	SEBS	PP	Transmittance	Haze
TPO1		0			20.9	79.3
TPO1-N1	95wt%	5wt%			42.8	70.0
TPO1-N2	90wt%	10wt%			35.9	73.1
TPO1-N3	80wt%	20wt%			31.3	72.3
TPO1-N4	70wt%	30wt%			28.6	73.2
TPO1-S1	90wt%		10wt%		27.9	76.8
TPO1-SN1	80wt%	10wt%	10wt%		36.9	71.5
PP-S				100wt%	80.4	11.1
PP-S-N1		10wt%		90wt%	42.7	63.3

Figure 6.1 (a) (b) (c) show SEM micrographs of fractured surface of neat PP, TPO1, and TPO1- CaCO_3 nanocomposite. Compared to PP with a relative uniform cross-section, TPO1 showed the nature of dispersed rubber particles as expected. With addition of 10wt% CaCO_3 , the particle size has been significantly reduced as shown in Figure 6.1(c). This may

be associated with the increased viscosity and shear force during compounding, The decreased rubber phase could act

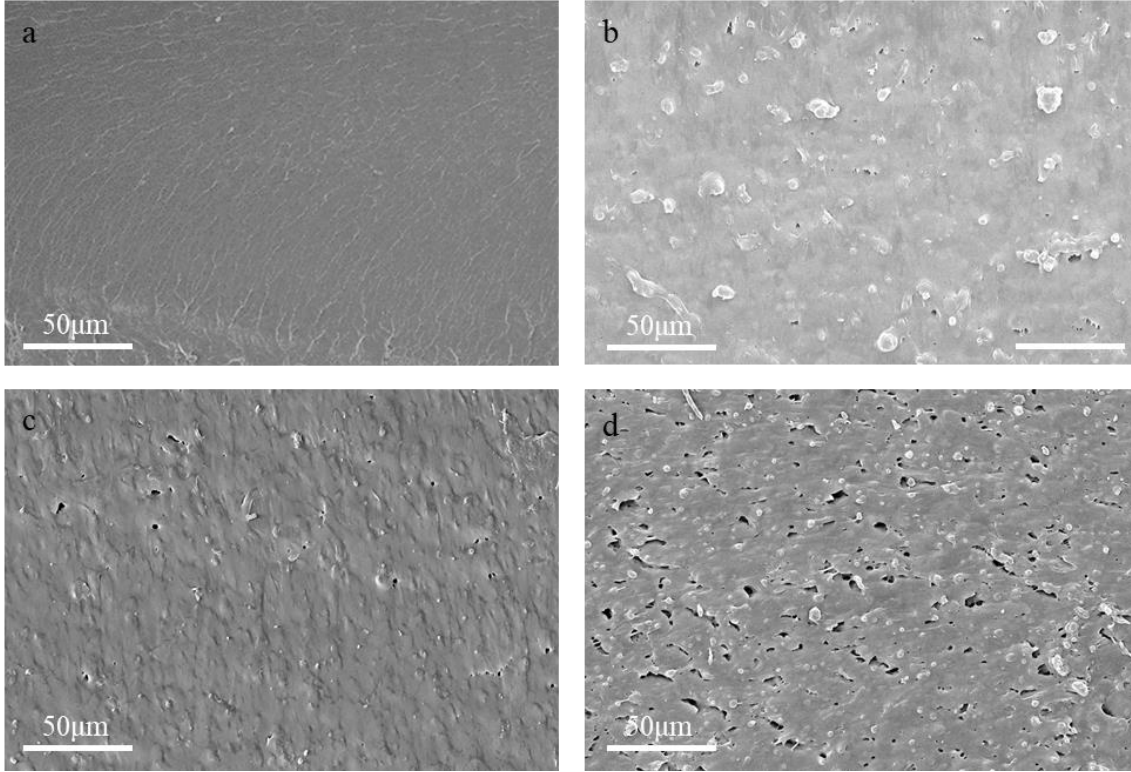


Figure 6.1 SEM of fractured cross section of injection molded samples (a) PP (b) TPO1 (c) TPO1-N2 (d) TPO1-S1.

6.3.2 Contact Angle

For TPO1 with CaCO_3 additive, it is crucial to investigate the location of nanoparticles. The preferential location of the clay in the polymer blend can also be estimated by the difference between the interfacial tensions of the components due to the tendency for reaching a minimum interfacial energy [176]. The wettability parameter, ω , can be used to predict the equilibrium location of clay in a mixture of fluids,

$$\omega_a = \frac{\gamma_{fA} - \gamma_{fB}}{\gamma_{AB}} \quad (6.1)$$

Where γ_{fA} is the interfacial tension between fillers and phase A, in this case, PP matrix phase,

γ_{fB} is the interfacial tension between fillers and phase B, disperse rubber phase and γ_{AB} is the interfacial tension between PP and rubber phase. For If $\omega < -1$ then clay is located in phase A, PP matrix phase, for $\omega > 1$, clay is predicted to locate in phase B, rubber phase. The solid particles are at the interface of the phases, if $-1 < \omega < 1$, clay is predicted to locate at the interface. The interfacial tension is determined from geometric mean equation of Wu[177]:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2 [(\gamma_1^d \gamma_2^d)^{1/2} + (\gamma_1^p \gamma_2^p)^{1/2}] \quad (6.2)$$

where, γ_1 and γ_2 are surface tension of components 1 and 2, γ_1^d and γ_1^p are their dispersive parts and γ_2^p and γ_2^p their polar parts.

The surface tensions of polymer components were calculated using contact angle θ , measurements according to Owens-Wendt equation with both polar and no polar liquid.

$$\gamma(1 + \cos\theta) = 2(\gamma_l^d \gamma_l^p)^{1/2} + 2(\gamma_s^d \gamma_s^p)^{1/2} \quad (6.3)$$

$$\gamma_l = \gamma_l^d + \gamma_l^p \quad (6.4)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (6.5)$$

Figure 6.2 showed the contact angle measurements of PP and CaCO_3 with water and diiodomethane and thus the surface tension and its dispersive component and polar component can be obtained. However, since the rubber phase in TPO1 remains unknown, we will have to select different rubber phase for calculation, and the result showed that. For EB rubber, the CaCO_3 is predicted to be located in PP phase, for EPDM, it will be at interphase, for EOC rubber, it is predicted to locate preferentially in rubber phase. Although this is a just theoretic calculation, but it provides informative prediction. At later stage of this research, with customized TPO, all phases are confirmed. It is expected this calculation will provide more reliable prediction.

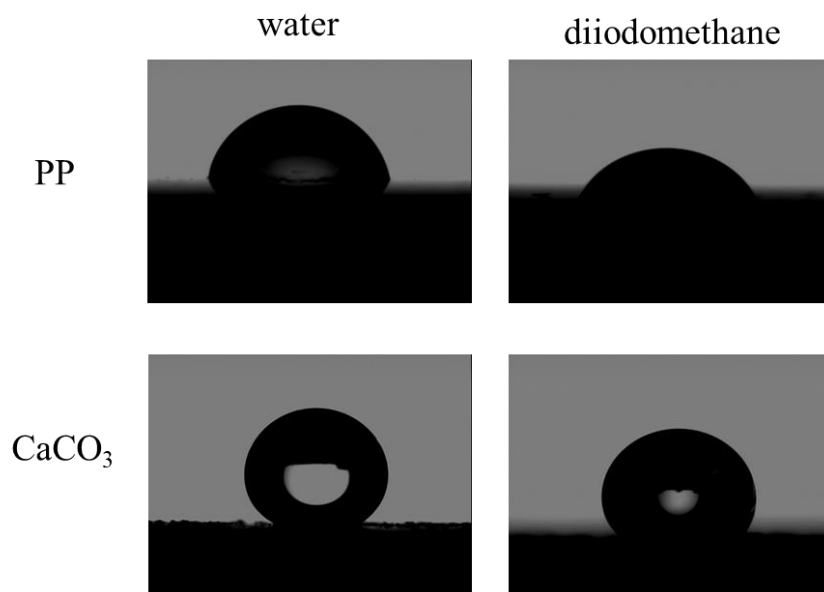


Figure 6.2 Contact angle measurements: Top row, PP ; Bottom row, CaCO₃.

6.3.3 Effect of SEBS on TPO1

As shown in Table 6.1, addition of external SEBS into TPO1 improved the optical performance with increased transmittance and decreased haze. The SEM micrographs of the cross-section is also shown in Figure 6.1(d), Compared to TPO1 as shown in Figure 6.1(b), apparently, the dimension of disperse rubber particles were reduced which can explain the improved optical. In addition, for achieving high clarity in mixed system, the refractive index in different components need to be close. The refractive index of PP is 1.49 while the refractive index of SEBS is 1.43 which may also help with optical improvement. Furthermore, as shown in Table 6.1, the best optical property improvement was achieved when incorporating both 10wt% CaCO₃ and 10wt% SEBS.

6.3.4 TPO with selected PP, rubber and additives

Figure 6.3 showed commercial grade TPO1 and 3 representative TPO blend with selected PP and rubber phase with or without nanoclay additive. Clearly, TPO1 is opaque while

other 3 are translucent. The optical measurement results as well as mechanical properties are shown in Table 6.2. In accordance with photo observation, the transmittance was increased, and haze was decreased in all 3 TPOS. Comparing TPO4 to TPO3, adding nanoclay decreased the haze, i.e. increased the sharpness. The flexural modulus was also improved with slight decrease in impact strength.

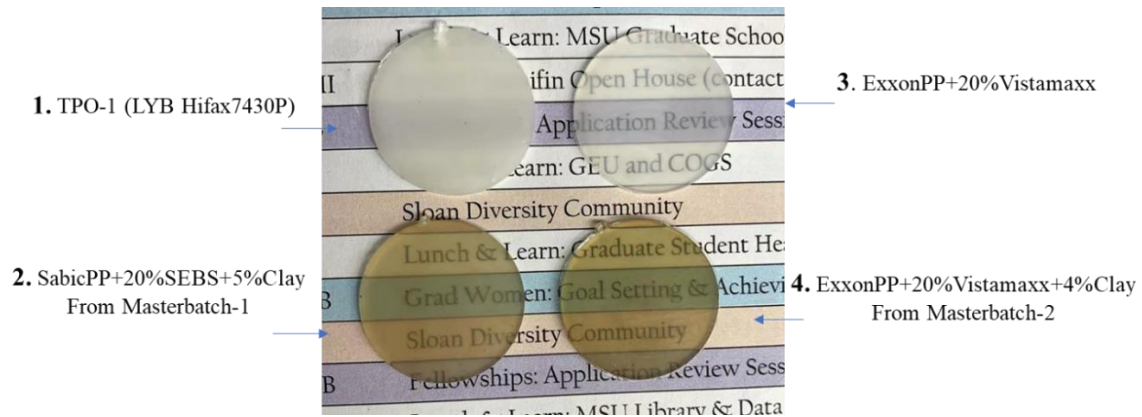


Figure 6.3 Comparison of 3 representative TPO with selected composition compared to commercial TPO1.

Table 6.2 Optical and mechanical properties of selected TPO.

	Transmittance	Haze	Flexural modulus MPa	Impact strength KJ/m ²
TPO1	20.9	79.3	1003	9.1
TPO2	52.0	19.0	1660	13.1
TPO3	63.0	25.0	718	9.4
TPO4	51.0	17.0	1112	8.7

6.3.5 Effect of thickness

A customized TPO nanocomposite with 6wt% nanoclay has been selected for preparing injection molded specimen with various thickness. Figure 6.4 shows a photo of physical appearance of injection molded samples including 1.5 mm disk samples from DSM mini

injection molder as well as 2 mm, 3 mm, 4 mm plaque samples molded from an industrial scale injection molder. Upon visual inspection, the transmittance decreases as thickness increases.

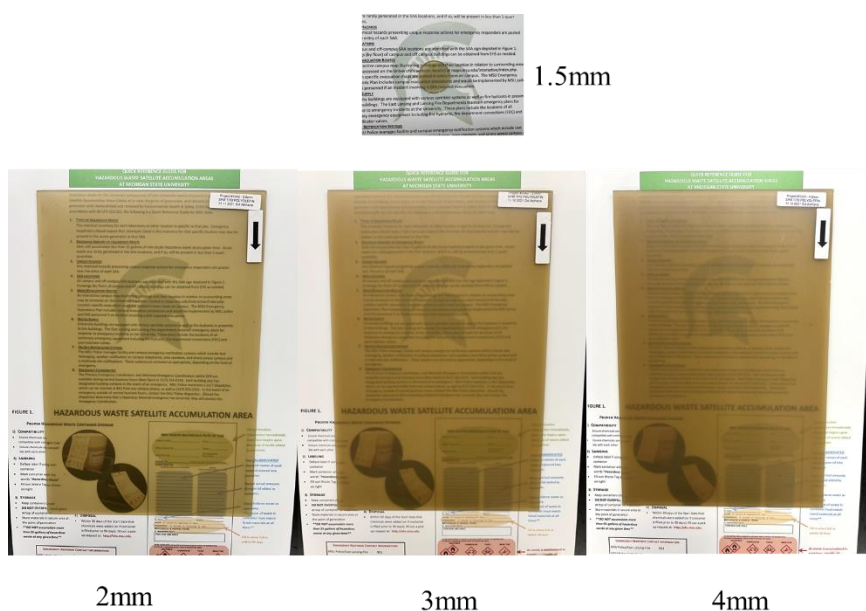


Figure 6.4 Photo of TPO nanocomposite R with various thickness, top 1.5mm; bottom, from left to right, 2mm, 3mm, 4mm.

A quantitative analysis of transmittance and haze as a function of thickness has been plotted in Figure 6.5 Transmittance and haze as a function of sample thickness. Clearly, transmittance decreased, and haze increased proportionally with increasing thickness. From 3mm to 4mm, there is a change in the slope due to the fact that the scattering effect was too large, and the effect of increasing thickness is insignificant. Nevertheless, this could help us select the appropriate sample thickness depending on target clarity.

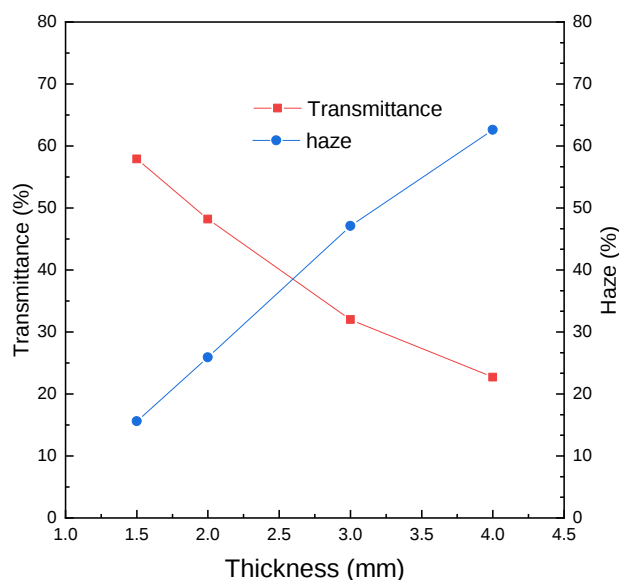


Figure 6.5 Transmittance and haze as a function of sample thickness.

6.4 Conclusions

Addition of nano CaCO_3 has shown to improve the optical property in TPO system with an optimal of 5wt%. Addition of SEB also helped improve the optical performance. A synergistic effect with both additives were also observed. SEM revealed that reduction in particle size of dispersed rubber phase accounted for such optical improvement. Furthermore, a series of customized TPO with various grade of selected PP and rubber phase were also fabricated. The effect of thickness on optical performance of TPO clay nanocomposite was also revealed. Current results have confirmed the promising potential of the two strategies 1. nanoparticle, 2. external clarifier, in obtaining translucent TPO.

Chapter 7. Conclusions and Recommendations

7.1 Biaxially oriented nanocomposite film

7.1.1 Conclusions

Simultaneous biaxially oriented polypropylene clay nanocomposite films were successfully prepared with an area stretching ratio of 7×7 without any breakage. Final film presented high clarity. Highly intercalated and partially exfoliated nanocomposite morphology was confirmed from TEM and shear rheology analysis. Biaxial stretching increase the delamination level and promoted higher in-plane orientation of clay platelets, which is advantageous in packaging applications. The incorporation of the silane-treated organoclay also increased the melt strength, storage modulus, mechanical robustness, and barrier property in BOPPNC compared to base BOPP, demonstrating the superb reinforcing effect. WAXD and SAXS revealed that the original lamellae were transferred in to longer and thinner crystallite after biaxial stretching. Addition of nanoclay further increased the long period and the lamellae thickness of these lamella crystallite. BOPPNC film showed a more balanced elongation to break ratio, which could be correlated to improved isotropic in-plane crystalline orientation as observed by WAXD and 2D-SAXS. The extent of improvement in oxygen barrier between unfilled and filled samples was more pronounced after biaxial stretching, which is in accordance to further improved nanolayer delamination and orientation as found after biaxial stretching.

Furthermore, different characteristic biaxial deformation behaviors of polypropylene clay nanocomposites when subject to sequential and simultaneous biaxial stretching were compared. Under selected processing conditions, it was found during simultaneous biaxial stretching, the stress-strain curves of both PP and PPNC along MD and TD showed a typical

ductile behavior with initial yielding followed by a softening plateau and a strain hardening. On the other hand, during sequential stretching along MD, a less typical yield along with a much broader softening plateau and no strain hardening was present. Along TD, absence of yielding point became more distinct with a rubbery trend and a steadily increased stress with increasing strain. Moreover, there is a significant rise in overall stress levels for a given stretching ratio during sequential stretching compared to that in simultaneous stretching. The effect of other processing parameters including stretching rate and temperature on stretching behavior was also revealed. Strain rates affect the deformation behavior on a various scale depending on the stretching mode but the effect of stretching temperature is consistent and more dominant. 2D SAXS revealed the different crystal structure development from extruded precursor to biaxially oriented films. Simultaneous stretching resulted in more isotropic while sequential stretching led to a preferential orientation of lamellae along stretching direction especially along TD. Moreover, long period of lamellae in sequentially stretched films were found to be slight larger than that of simultaneously stretched film. For macroscopic properties, sequentially stretched nanocomposite films exhibited less balanced mechanic property compared to simultaneously stretched composite but addition of nanoclay seems to abate such anisotropy. The barrier performance of simultaneously stretched films is slightly better than sequentially stretched films. These properties can be correlated to their crystal structure.

7.1.2 Recommendations

The structure evolution of BOPPNC during the stretching process remains unrevealed in current research. It is also essential to understand how the polymer chains and the organoclay nanolayers respond at different stages of biaxial orientation. These include the morphology evolution of crystalline and amorphous phase, orientation and dispersion of clay

nanolayer at various strain level. In order to probe the structure evolution, a series of film with incrementally controlled stretching ratio would be desired. If possible, an in-situ characterization capability during biaxial stretching should be utilized. This will also help confirming potential temperature change such as adiabatic heating during biaxial stretching especially with high strain rate.

For comparison between simultaneous and sequential biaxially stretched nanocomposite film, the area stretching ratio in two cases was selected as 7×7 and 5×9 with the purpose to simulate the processing conditions in practical industrial process such as double boule or tenter frame. This discrepancy between our current equal simultaneous biaxial and asymmetric sequential stretching introduced more complexity, a comparative study of the two stretching modes with same area stretching ratio may also be conducted. Additionally, the influence of other processing parameters including stretch temperature and strain rate for sequentially stretched samples has not been revealed due a limited instrumental access to date. As a result, only the structure and property of films under a fixed stretching temperature and rate in this processing mode was investigated. To completely understand different effect with presence of clay in different stretched films, nanocomposite films under various processing conditions in sequential stretching also need to be investigated.

On the other hand, BOPP film has been the mainstream in dielectric capacitor film for energy storage application. Incorporating organoclay has been shown to improve the on the dielectric and energy storage properties of polypropylene nanocomposites [178]. The nanocomposites are reported to possess a relatively high dielectric constant of 3.35 and an extremely low dielectric loss of 0.0012 at 1000 Hz. These nanocomposite also exhibited a desired discharged energy density and a superior charge–discharge efficiency which were

favorable for film capacitor films. However, these results were obtained based on unstretched PP while BOPP is the actual form used for capacitor film. Since our results in this dissertation have showed a great potential for fabricating BOPP nanocomposite films, it would be intriguing to investigate their dielectric and energy storage properties.

To conclude, the future work could be: i) investigating the structure evolution during processing of BOPP nanocomposite film with incrementally increased stretching ratio; ii) comparing the difference between the two stretching modes, i.e. simultaneous and sequential biaxially locations under same stretching ratio in MD and TD; iii) completing the structural and property characterization and understating their relation in comparison between sequential and simultaneous biaxial stretching; iv) it would be intriguing to investigate the dielectric and energy storage properties of these BOPP clay nanocomposite films.

7.2 A look into sequential biaxially stretched nanocomposite film from a continuous line

7.2.1 Observation and discussion

In our experimental trials, two instruments were used for fabricating sequential biaxially stretched nanocomposite films, a KARO IV laboratory stretcher and a continuous tenter frame production line. While the films produced from the Karo IV stretcher are clear, however, for sequentially stretched BOPP nanocomposite films produced via the continuous production line, some opacity was observed. It is also found such opacity appeared only during the second transverse stretching step. An optical microscopy was used to examine all the films from a top-view. Figure 7.1 (a) (b) showed a representative films produced via continuous tenter frame production line with low and high magnification respectively. Apparently, the microscopy image shows agglomerates with presence of white regions around sphere particles indicting cavitation regions, which accounts for the opacity in the film.

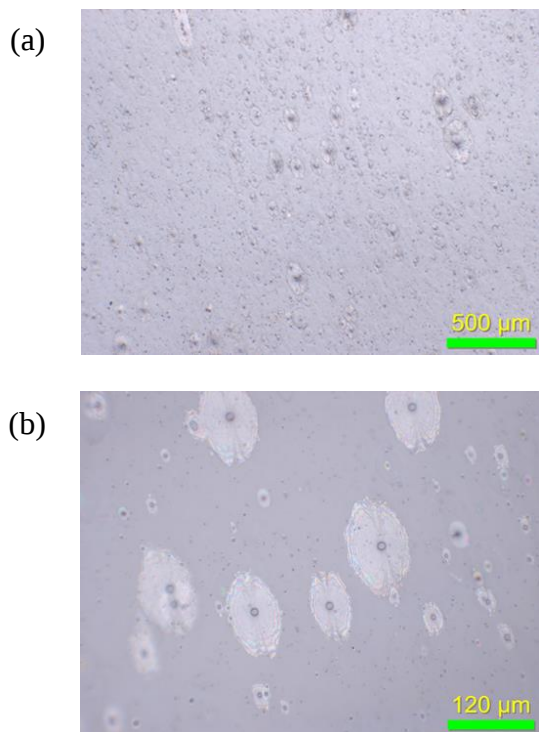


Figure 7.1 Optical micrographs of top view of sequentially stretched BOPP nanocomposite film with 5wt% loading from continuous production line: (a) 5X lower magnification; (b) 20X higher magnification.

From the optical microscopy image of the cavitated films, it is indicated that the cavitation occurs around the filler particles. To further confirm this observation, SEM was conducted by looking at the cryo-fractured cross section area. The results are shown in Figure 7.2 with (a) (b) (c) correlated to the cross section of the transparent film, cavitated film with voids around micron sized and submicron sized clay particles, restively. SEM images clearly show that a debonding occurs at the interface between the stretched polymer matrix and filled particles. It has been known that debonding produces voids in the stretched film [3].

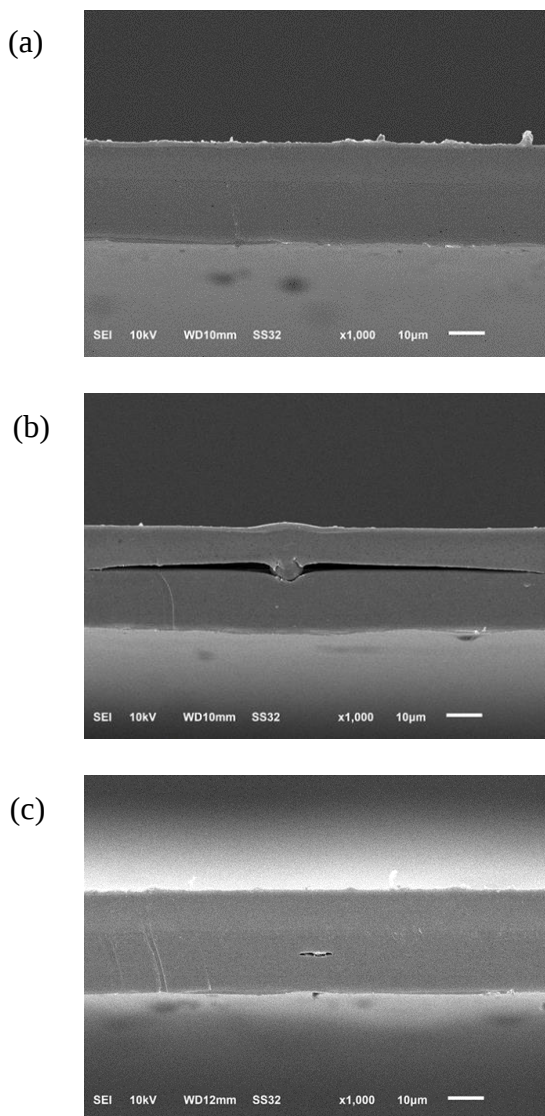


Figure 7.2 SEM micrographs of BOPP nanocomposite film from cross-section view: (a) clear film from equal-biaxial simultaneous stretching; (b)(c) voids of different cavitation size in films from asymmetric sequential stretching, the tenter frame production line.

Debonding in particulate filled composites under tension has been of large interest in literature [179–186]. It occurs due to the lack of adhesion between the polymer chains and filled particle. During the stretching process, macroscopic stress applied to the polymer matrix could not be transferred to the rigid particles causing local stress concentration around the edges or tips of the particle. When the potential energy near the particles exceeds the work of

adhesion, voids will be initiated. The dimension of interfacial void will be elongated with increasing stretching ratio until the void length reaches a critical defect value, crack will be propagated leading to fracture. Although with voids, the maintained film integrity indicated that stretching ratio used in this particular tenter frame production line did not cause the elongation of void exceeding the critical size of defect dangerous for breakage.

Vollenberg et al. [179] derived an equation based on potential energy around a spherical inclusion to create new surfaces. Pukánszky and Vörös [180] proposed a model based on energy equalities. Both models suggested that debonding stress was proportional to the reciprocal root of the particle radius particles, i.e., particles with larger size will debond under a lower stress. Coexistence of voids with different dimension is confirmed from both the optical microscopy and SEM image. It is inferred that larger voids formed at small TD stretching ratio while the smaller one generated at larger strain during biaxial stretching.

Compared with simultaneous biaxial stretching, the stress levels in sequential stretching were considerably higher at the same strain and increases steadily with increasing stretching ratio. This means a higher risk of debonding. Moreover, some researchers reported that the debonding process happens primarily in the elastic region before the yielding point of the polymer is reached [185,186]. In previous discussion, a lack of characteristic yielding point has been found in sequentially stretched films, especially in second TD stretching step. This continuous increment of stress accumulation in TD stretching in sequential biaxial orientation may account for the occurrence of deboning in this tenter frame line. However, due to a lack of accessible parameters in this production line, it remains unclear of the actual stress levels accounted in traverse stretching step. Moreover, due to the heat transfer limitation, there may be a significant difference between set temperature and the actual film temperature. Such

difference can be more pronounced at commercial production line with high manufacturing speed as the film has less residence time [3]. Nevertheless, taking account of the different stress-strain behavior in simultaneous and sequential biaxial stretching, the potential of debonding occurrence in the latter was considered to be higher due to the absence of characteristic yielding and the increased level of stress during sequential biaxial stretching. When it comes to asymmetric sequential stretching process such as tenter frame, more attention needs to be paid on the debonding potential between the stretched polymer chains and filler particle.

7.2.2 Recommendations

We report observation of cavitated regions in asymmetric sequentially stretched film from a continuous tenter frame production line. It is speculated that characteristic sequential biaxial stretching behavior may play a role and requires further investigation. For further investigation of cavitation issue during asymmetric sequential stretching from commercial line, the capability capturing processing parameter is needed which can then be mimicked via the laboratory stretched. Also, it needs to be confirmed if debonding only occurs during the transverse stretching step around submicron sized nanolayer stacks, which will also require sample obtained from the first MD stretching step.

To conclude, the future work could be: i) obtaining the processing condition in continuous line; ii) confirming the stage where debonding occurs; iii) conducting a sequential stretching mimicking the continuous production line with controlled processing parameters to find out the effect of different processing parameters on debonding potential, whether a dominating parameter exist or a combination of different parameters.

7.3 Nanocomposite Foam

7.3.1 Conclusions

In this study, foamability of PP clay nanocomposites is evaluated with a batch foaming apparatus using supercritical CO₂. High melt strength and addition of nanoclay helps the nanocomposite foam cell to withstand high expansion force allowing for a relatively larger cell size capability. Nanoclay also increased the cell density significantly. Combining both factors, nanocomposite foam exhibited an ultra-high expansion ratio as well as a fine cell structure compared to base PP foam. The dispersion and alignment of nanolayer was compared to unfoamed samples and it was found the foam expansion induces enhanced delamination and orientation of clay nanolayers. Strain hardening behavior is confirmed in the nanocomposite via extensional rheology analysis. Biaxial stretching at elevated temperature close to batch foaming temperature also showed high stretchability of PP clay nanocomposites and the maximum area stretching ratio was found can be correlated to the maximum expansion ratio. Mechanical compressive test demonstrated high compressibility and maintained strength in nanocomposite foam. These results clearly demonstrate the possibility to achieve high expansion ratios in TPO composites consisting ternary systems of a crystalline PP matrix, a dispersed elastomer, and a filler in a next-phase study.

7.3.2 Recommendations

In current study, only certain conditions were selected to probe the formability of PP and PP clay nanocomposite with an emphasis to achieve highest expansion ratio if possible. For a more systematic study, effects of temperature and pressure on the expansion ratios and cellular morphology of the nanocomposite foams need to be investigated. In the current setup, supercritical CO₂ was maintained via addition of dry ice. In order to have better control of the

saturation pressure, it is recommended to use a pressurized CO₂ gas tank as the source. A better control of depressurization rate is need as well. Also, the correlation between crystallization and foaming need also to be clarified with a possible investigation on the crystallization behavior before and after foaming. In particular, the crystallization behavior of nanocomposite under supercritical CO₂ also needs to be studied if possible. This is important to clarify the contribution from either melt or semi-solid state.

It is expected that the implementation of clay nanolayers can lead to a reinforcement in the mechanical of foams, by strengthening the cell walls. However, there is a lack of controlled comparison in our current experiment. The reinforcement effect can only be verified between PP and PP nanocomposite foams with same expansion ratio, which can be achieved via controlling the foaming condition.

Although current study is focused on PP and PP nanocomposite foam, it also provide fundamental information for foaming of thermoplastic polyolefin (TPO) which is essentially composed of a continuous PP embedded with dispersive elastomeric phase. In fact, TPO foam has been widely used especially gains more and more prevalence in automotive industry as both exterior such as bumper fascia and interior such as dashboards and panels. It would be of huge interest to investigate TPO nanocomposite foam with nanoclay additives via this supercritical batch foaming method.

Furthermore, Lataillade and co-workers [164] investigate the compressive behavior of expanded polypropylene foams under both quasi-static and dynamic compression. The foam they compared are of same density by different microstructure. It is found larger cells (longer and thicker cell walls) are more prone to bend or buckle during quasi-static loadings, but under dynamic loadings they tend to be stronger due to the micro-inertia effect which makes them

more difficult to bend or buckle. In our experiment, only the quasi-static compressive behavior is investigated, therefore it is of interest to look at the dynamic compressive behavior as well .

To conclude, the future work could be: i) investigating the effect of temperature, pressure and depressurization rate on PPNC foaming; ii) understanding the correlation between crystallization and foaming, if possible, under supercritical CO₂ condition; iii) validating the reinforcement effect of nanoclay on foam mechanical properties by comparing PP and PPNC foam with same expansion ratio; iv) investigate the potential in TPO nanocomposite foam with similar methodology; v) investigating compressive behavior of highly-expanded nanocomposite foam under dynamic loadings.

7.4 TPO nanocomposite

7.4.1 Conclusions

Current results demonstrated promising potential of the two strategies 1. nanoparticle, 2. external clarifier, in obtaining translucent TPO. It is found that addition of nano CaCO₃ increased transmittance and decreased haze in TPO blend. Addition of SEBS also helped improve the optical performance. A synergistic effect was also revealed with both additives incorporated. SEM revealed that reduction in particle size of dispersed rubber phase accounted for such optical improvement. Furthermore, a series of customized TPOs with various grade of selected PP and rubber phase were also fabricated. Optical and mechanical performance were evaluated. The effect of thickness on optical performance of TPO clay nanocomposite was also revealed.

7.4.2 Recommendations

In current work, both CaCO₃ and nanoclay particles have been selected as the filler materials respectively. Yet it remains to be understood how the geometry of fillers, i.e.,

spherical or platelet will influence the microstructure and macroscopic property of TPO nanocomposites, especially on optical and mechanical properties. With this regard, a recommendation would be to investigate the addition of fillers with different geometry based on a model TPO system with controlled PP matrix and dispersed rubber phase. Dispersion and location of these nanoparticles and the effect on blend morphology need to be investigated. In addition, it is reported that coexistence with two types of fillers, such as talc and calcium carbonate (CaCO_3) in hybrid PP composites has achieved successful synergistic hybridization effect with enhancement in both flexural strength and impact strength [173]. Thus it would be intriguing to investigate the effect with presence of nanoparticles with different geometry nature.

To conclude, the future work could be: i) continuing in investigation of TPO nanocomposite with various combination of nanofiller and external rubber additive for optimal performance; ii) validating the location of nanofillers via TEM, whether in matrix phase, rubber phase or interphase; iii) investigating the effect of fillers with different geometry, such as spherical or platelet on the optical performance and mechanical property of TPO nanocomposite, and if a synergistic effect may exist if both fillers incorporated.

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