

**USE OF SUPERCRITICAL CARBON DIOXIDE
IN THE PROCESSING OF
THERMOPLASTIC ELASTOMER NANOCOMPOSITES**

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BY

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TITLE: Use of Supercritical Carbon Dioxide in the Processing of
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ABSTRACT

Polymer-layered silicate (PLS) nanocomposites are of great interest presently due to their significant enhancement of properties compared to conventional polymeric materials. However, achieving a high extent of exfoliation, which refers to the complete separation and uniform dispersion of clay layers, is a key challenge in the preparation of PLS nanocomposites, particular for non-polar polymers like polyolefins. Recently, several novel processing technologies utilizing scCO₂ as an exfoliation aid have been developed. But how to achieve an optimal processing method by which fully exfoliation occurs with the aid of scCO₂ has not been fully studied.

A novel clay-CO₂ injector apparatus was designed and constructed for this project in order to maintain the organoclay in suspension with scCO₂ during its melt compounding into a nanocomposite. Thermoplastic polyolefin elastomer (TPO) based nanocomposites were prepared by three methods: 1) directly injecting the CO₂ into a twin screw extruder (TSE); 2) injecting an organoclay-CO₂ suspension along with its compatibilizer into a twin screw extruder; and 3) injecting the organoclay-CO₂ suspension into a single screw extruder (SSE). Under Method 1 both as-supplied organoclay and a previously scCO₂-pretreated organoclay (from batch) were tested, while for the other two methods only the as-supplied material was used. The structure and properties of the resultant nanocomposites were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), rheology and mechanical testing.

It was found scCO₂ has a great influence on the morphology of clay within TPO nanocomposites. When preconditioned in scCO₂, chain mobility of surfactant within clay

interlayers increased and led to further cation exchange reactions, thus resulted in an expansion in interlayer spacing and greater chance for penetration of large polymer specimen. It was shown in XRD patterns and TEM graphs that nanocomposites prepared using these pretreated organoclays (s-C20A) improved the degree of exfoliation over those based on as-supplied organoclay, in the absence of CO₂. On the other hand, the *clay-CO₂ injector* could also be beneficial for achieving an exfoliation structure. With increasing CO₂ pressure, the mobility of surfactant/compatibilizers chains increased, allowing greater intercalation of matrix chains and further delamination under shear flow. The greatest exfoliation structure so far was achieved by maintaining the C20A/CO₂ suspension above the critical pressure of the gas during first-pass melt compounding in a single screw extruder then following with a second-pass through a twin screw extruder which provided sufficient shear stress for further exfoliation without the plasticizing effect of CO₂. Both pretreating clays and clay-CO₂ injection approaches showed improvement in clay dispersion over conventional nanocomposites melt compounding method. However, this improved exfoliation structure did not directly bring on improvement of rheological and mechanical properties. A possible thermo oxidative degradation was considered to be responsible for the reduction in rheological and mechanical properties.

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SSE Single screw extruder

TSE Twin screw extruder

Symbols

T_c Critical Temperature

P_c Critical Pressure

2θ X-ray diffraction angle in Bragg's Law

H Height of the core in angle of repose test

D_A Diameter of the cone in angle of repose test

d Internal diameter of the funnel nozzle

λ Angle of repose

s Maximum shear stress

σ_n Nominal normal stress

ϕ Angle of internal friction

C Cohesion

Q Flow rate

τ_w Shear stress at the wall

ΔP Pressure drop

η Viscosity

$\dot{\gamma}$	Shear rate
n	non-Newtonian index
G'	Storage modulus

CHAPTER 1 INTRODUCTION

1.1 Background

During the last decade, the fast development of the automotive industry globally has led to significant environmental challenges related to fuel efficiency and carbon dioxide emissions. Among many automobiles design parameters, vehicle weight was found to be a key factor for significantly reducing the fuel consumption and carbon dioxide emissions. Generally, a 10% weight reduction can lead to 3-7% improvement in fuel saving [Keoleian, et al. 1997]. For this reason, plastics have become alternative materials to conventional metals due to their relatively low density. Polypropylene has become one of the most popular automotive plastics in recent years because of its property versatility, inexpensive price and lightweight (with a specific gravity of 0.89-0.91). In 2003, polypropylene-based resins have made up more than 35% of all thermoplastics used on North American automobiles [McAuley 2003].

Although providing weight advantages, the usage of plastic materials in body panels and structural components is limited since usually plastic materials can not provide the same level of mechanical properties as conventional metals. Polymer based nanocomposites, a new class of materials where nanofillers are uniformly dispersed within a polymer matrix, represent an emerging class of materials well suited to the automotive industry due to the multiple fold increase in mechanical properties provided by the nano-scale filler with almost negligible increase in part weight. Of the various nanocomposites currently being developed in the literature, polymer layered silicate (PLS) nanocomposites has become the most popular since clays are inexpensive and readily accessible. The first commercialized example, a Nylon-6/montmorillonite (MMT) nanocomposite produced

by the Toyota research group stimulated the intensive investigation into these novel materials [Usuki et al. 1993]. In this decade, General Motors has become the leader in utilizing this class of nanocomposites. The first commercial auto exterior use of a thermoplastic polyolefin elastomer (TPO) nanocomposite was in the step-assist of their 2002 GMC Safari and Chevrolet Astro van. More recently, these TPO-based nanocomposites were announced for use in the side body paneling of their 2004 Chevy Impala and 2005 GM Hummer H2 SUT [Bhattacharya et al. 2007]. These applications reveal a great potential of this class of materials. However, industrial practise with these materials remains very limited mainly due to the low performance/cost ratio for these nano-materials.

The mechanism of formation for PLS nanocomposites involve guest intercalation and exfoliation. *Intercalation* refers to polymer chains diffusing into the interlayer regions of a clay's structure forcing the spacing between adjacent platelets to increase. *Exfoliation* is the uniform dispersion of these generated platelets within the polymer matrix, in order to maximize the polymer-clay interfacial area. However, pristine layered silicates are only partially compatible with hydrophilic polymers and form no associations with non-polar resins [Aranda et al.1992]. In order to render the hydrophilic clay's surface oleophilic, an organic surfactant must be applied to the clay surface and this process is expensive. Even for these organo-coated clays, non-polar polyolefins such as TPO or polypropylene still do not exhibit the favourable enthalpic interactions required to overcome the entropic loss related to confining a polymer within clay interlayers, and thus intercalation is not favourable [Vaia and Giannelis 1997]. With the aid of polymeric compatibilizers such as maleated polyolefins, intercalation improves but fully exfoliation is still difficult to achieve [Kato et al. 1997]. As full exfoliation is necessary to gain the greatest improvement in physical properties of the final product [Alexandre et al.2000; Pavlidou et al.2008], newer technologies that aids exfoliation are needed.

Currently, some disruptive technologies such as the use of ultrasound irradiation [Lim et al. 2003], electrical fields [Lu et al. 2006], and supercritical CO₂ (scCO₂) [Nguyen and Baird 2007; Armstrong et al. 2007; Treece et al. 2006; Horsch et al. 2006] have been reported to improve the exfoliation of the clay. Among them, using scCO₂ as an exfoliation aid is most likely to meet the current industrial processing requirement due to its readily accessible critical condition and environmentally benign nature. During the processing of nanocomposites, supercritical CO₂ acts like a plasticizing/compatibilizing agent that aids exfoliation [Nguyen and Baird 2007]. Currently, there are three strategies for using scCO₂ in the compounding of nanocomposites reported in the literature. The first is direct injected gas into the polymer/clay melt [Treece et al. 2006]. The second is pretreating the organoclay in scCO₂ off-line, removing the material from the high pressure environment and then adding it into the melt [Horsch et al. 2006; Manke US patent # 6,469,073]. Finally there is injecting the organoclay within a supercritical suspension into the melt compounding process, with either the extruder being maintained above the critical pressure of the gas so that mixing occurs in the supercritical state [Rodgers et al. 2008 – GM patent] or the extruder operates at low pressure and the gas is allowed to phase separate from clay and polymer [Nguyen and Baird 2007].

1.2 Objectives

The research in this thesis focused on the participation of carbon dioxide in the processing of a TPO/clay nanocomposite as a means of adding value to the final product. This thesis investigated the current existing strategies for using scCO₂ as an exfoliation aids and tries to overcome the drawbacks in the previously mentioned methods above. The research consisted of :

- 1) Review the currently existing strategies using scCO₂ and develop a *clay-CO₂ injector* to i) inject clay into the polymer melt as a suspension with scCO₂ rather than being directly added as a powder; ii) maintain the suspension at critical conditions during compounding, iii) minimize the gas content in the

extruder so that the material is not foamed, and iv) achieve a optimal state for manufacture this TPO nanocomposites.

- 2) Evaluate all of the PLS nanocomposites processing methods using scCO_2 reported in the past five years by continuous processing of the nanocomposites in both a single screw extruder and/or a twin screw extruder.
- 3) Characterize the morphology, rheology and mechanical properties of the produced samples. The results of this study will be used to develop an optimal processing technology for producing fully exfoliated PLS nanocomposites.

The research in this thesis was expected to address the questions of scientific and industrial significance: 1) Does scCO_2 within the gas-laden molten nanocomposites improve the extent of exfoliation? 2) Does exfoliation significantly improve the end-use properties of the nanocomposites? 3) Do processing conditions have an important impact on the properties of the final product?

1.3 Organization of the thesis

This thesis is composed of five chapters. The first chapter is this introduction. The second chapter is a literature review which gives greater details on the structures/component of the PLS nanocomposites; the main processing methods and the current use of scCO_2 . The third chapter introduces the design and construction of a novel but simple *clay-CO₂ injector* apparatus. The fourth chapter details the processing methods for producing the different TPO-based PLS nanocomposites and discusses the results in detail. The final chapter gives conclusions and provides some future recommendation.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

There has been growing interest in polymer-layered silicate nanocomposites both in academic and industrial areas during the last decade. Nanocomposites are a class of materials where polymer matrixes are reinforced by nanoscale particles. Because of the high surface area and high aspect ratio of nanofillers, polymer nanocomposites will potentially exhibit significantly improved mechanical properties, barrier properties, thermal properties and flame-retardant properties compared to those of conventional filled composites. Among numerous nanofillers, layered silicates have been most widely used because these materials are readily available and their interaction chemistry has been intensely studied for a long time [Gorrasi et al. 2002]. In the automotive industry, polymer-layered silicate nanocomposites (PLS) are being developed to become a potential alternative to the conventional materials because of their relative low cost, similar or higher mechanical properties and more importantly, low weight. Weight savings are particularly crucial to recent automotive manufacturing practices since it correlates with fuel efficiency and carbon dioxide emission which are both significant global issues. The first commercial material of PLS nanocomposites in the automotive industry was a Nylon-6/montmorillonite (MMT) nanocomposite produced by the Toyota research group. The research group found that a very small amount of layered silicate loading (4.2 wt%) resulted in a significant improvement in thermal and mechanical properties [Usuki et al. 1993]. This introduction of a new advanced polymer material stimulated the motivation for greater investigation into PLS nanocomposites. Vaia and co-workers [Vaia et al. 1993] reported that a polymer matrix could be melt-mixed with the layered silicates in a more stable manner compared to solution intercalation. Melt intercalation, which meets the industrial requirement better than other methods, has

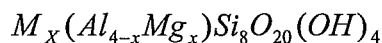
become the main stream for fabricating PLS nanocomposites due to simple processing, low cost and environmental friendly. Since then, the techniques of preparing nanocomposites have developed rapidly. Almost all types of polymers of different polarities have been investigated from polar polymers to non-polar polypropylene and different organic modifications have been applied to pristine layered silicate clay to improve their interaction with said polymer matrices.

2.2 Structures and components of TPO based nanocomposites

Thermoplastic polyolefins (TPO) refers to the polymer/filler blends where the polypropylene is modified by inorganic fillers such as talc and elastomeric components such as ethylene-propylene-diene terpolymer (EPDM), ethylene-propylene rubber (EPR), or an ethylene- α -olefin metallocene copolymer [Thompson and Yeung 2006]. In recent years, exploitation of TPOs in PLS nanocomposites has been extensive, particularly for the automotive industry where the material offers vast potential in exterior and interior part utilization. Such interest is spurred on by their relative low cost, low density, ease of processing and versatility in terms of properties and applications.

2.2.1 Structure and organic modification of layered silicate

The most commonly used layered silicate in PLS nanocomposites is montmorillonite (MMT), which belongs to the 2:1 phyllosilicates clay family. The general formula of MMT is given as follows:



where M refers to monovalent cation and x refers to degree of isomorphous substitution, usually between 0.5 and 1.3 [Giannelis, et al. 1999; Alexandre et al. 2000]. The crystal lattice of montmorillonite is made up of two-dimensional layers where a central octahedral sheet of alumina or magnesia is sandwiched between two silicon oxide

tetrahedral sheets. Oxygen ions are shared by both octahedral and tetrahedral sheets since these sheets are fused by the tip. The layer thickness is in the order of 1 nm, and the lateral dimensions of these layers are around 200 nm or even larger [Pinnavaia et al. 2000]. Thus, the aspect ratio of these layers (ratio length/thickness) is very high, sometimes with value more than 1000 [Beyer 2002]. Since these nanofillers are so small in actual size, they have a strong tendency to agglomerate rather than uniformly dispersed in a polymer matrix [Fischer, 2003]. In fact, these layers tend to stack, held together by Van der Waal forces, separated by 1 nm gaps. Each gap between sheets is referred to an *interlayer* or *interlamellar region* or a *gallery*. As the forces that hold the layers stack together is relatively low, it is easy for small polar molecules to intercalate into the layers and expand them. Due to isomorphic substitution (i.e. Al^{3+} replaced by Mg^{2+} or by Fe^{2+} , or Mg^{2+} replaced by Li^+) within the sheets there is a resulting negative charge at the surface that must be balanced. Charge balancing is provided by alkali and alkaline earth cations located in the interlayers, such as Na^+ and K^+ . These cations are exchangeable and the sum of the charges is referred to cation exchange capacity (CEC), which determines the ability of cationic surfactant that can be intercalated into the interlayers.

Virgin layered silicates usually contain hydrated ions such as Na^+ and K^+ . From the literature, only hydrophilic polymers such as poly(ethylene oxide) (PEO) [Aranda et al. 1992] or poly(vinyl alcohol) (PVA) [Greenland, 1963] are found to be compatible with the pristine layered silicates. For non-polar polymers like TPOs and polypropylenes, they are not miscible with these phyllosilicates clays because of unmatched chemical affinity. It is necessary to render the hydrophilic clay surface oleophilic by chemically modification so it may be compatible with non-polar polymer matrices. This chemically modification is called cation-exchange reaction, in which the hydrated interlayer cations (Na^+ , Ca^{2+}) are replaced by cationic surfactants such as quarternary alkylammonium or alkylphosphonium (onium) [Alexandre et al. 2000]. The modified clays exhibit lower surface energy and improved wetting characteristics with the polymer. In addition, the long organic chains of the surfactant, with positively charged ends, cover the surface of

negatively charged silicate layers, leading to an expansion of the interlayers [Kim et al. 2001]. Therefore, even non-polar polymers chains have the possibility to intercalate between the layers and then separate them. It is a generally held belief that the larger the original interlayer spacing of an organically modified clay, the more readily the polymer matrix can diffuse (intercalate) within its structure.

The interlayer spacing of organoclay is dependent on two parameters, the surfactant chain length and cation exchange capacity (CEC) of the layered silicates. Generally, the longer the organic chains and the higher CEC of the clay, the further expansion in the interlayers will take place. Zilg et al. [2000] found that organoclay interlayer distances expanded significantly when the chain length of the alkyl group of the ammonium cation exceeded 6 carbon atoms. Work by Lagaly et al [1986], who prepared organoclay with different alkylammonium chain lengths and clays with different CEC, showed the same trend in their results. The authors also proposed the interlayer spacing was dependent on the arrangement of alkyl chains, which is shown in Figure 2.2.1. With increasing of chain length for a n-alkylammonium, the arrangement of chains transitioned from a monolayer to a bilayer with larger interlayer spacing. Moreover, the higher cation exchange capacity of clay combined with the use of dialkyl or trialkyl further expanded the interlayer, leading to a paraffin-type monolayer or bilayer structure.

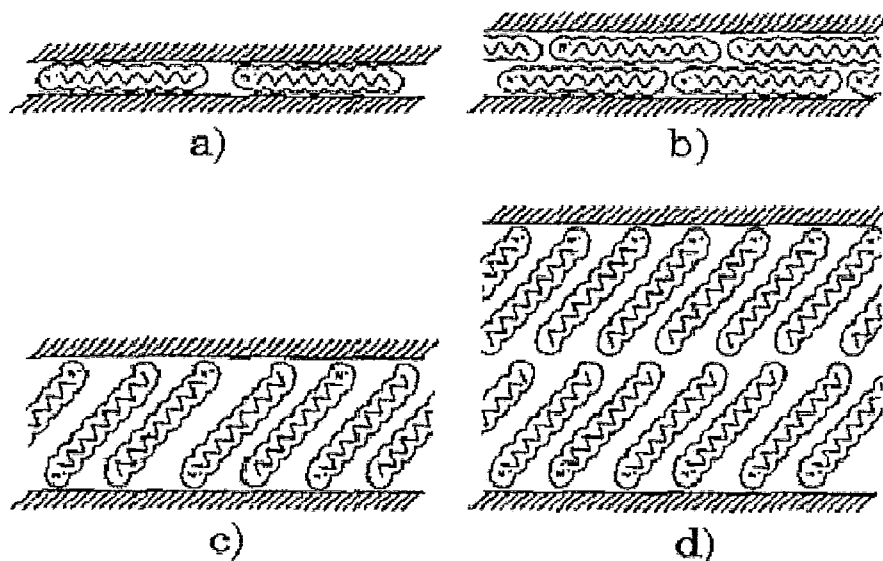


Figure 2.2.1 Alkyl chain aggregation in layered silicates: (a) lateral monolayer; (b) lateral bilayer; (c) paraffin-type monolayer and (d) paraffin-type bilayer [Vaia et al. 1994; Alexandre et al. 2000]

Recently, some researchers offered new insight into the arrangement of cationic surfactant within the clay structure. Deng et al. [2003] believed that the surfactants were not always fully intercalated into the interlayer of the clay. Instead, these surfactants might be located at the edge of the silicate sheets due to absence of a cation moiety. He et al. [2006] pointed out that there are three molecular environments for the surfactant within the clay: 1) intercalated into the clay interlayers by cation exchange and electrostatic interaction; 2) physically adsorbed on the external surface of the clay; 3) located within the clay interlayer by the hydrophobic bonding with the aliphatic tails of the surfactant. It was found that intercalated surfactant were most stable whereas physically adsorbed species were most easily to remove, which meant insufficient stability.

2.2.2 Compatibilizers: maleated polypropylene

A key step to preparing PLS nanocomposites is the intercalation of polymer chains into galleries between layered silicates [Vaia et al. 1997, 2001]. Vaia et al. [1997] proposed a mean-field, lattice-based thermodynamic model regarding the formation of PLS nanocomposites. The authors pointed out that since the interlayer of silicate is in the order of 1 nm, which is smaller than the radius of gyration of most polymers, there must be a large entropic barrier which restrains the polymer chains from intercalating into the interlayers and interacting with the clay. This entropic loss due to confinement of the polymer within clay galleries is partially compensated by an entropy gain, which is due to layer separation and greater conformational energy of the aliphatic chains of the alkylammonium cations. But this compensation is not enough and the entropy remains negative. In order to overcome the entropic penalty, there must be favourable enthalpic interactions between polymer and clay. However, polyolefins (particularly TPOs and polypropylene), unlike other partially polar polymers, are not able to present such favourable enthalpic interactions. Thus, it is extremely difficult to form homogeneous and thermodynamically stable TPO based nanocomposites because of their incompatibility with the polar inorganic fillers.

To overcome the unfavourable approach between non-polar polyolefins and polar layered silicate, a polymeric compatibilizer must be introduced into the nanocomposites system. The compatibilizer applied in PLS nanocomposites refers to a class of functionalized polymer whose backbone structure is similar to the matrix resin but containing incorporated functional group suited to interaction with organically modified clays. That is, this compatibilizer is compatible with the organoclay and also partially miscible with the polymer matrix. The first application of compatibilizers in PLS preparation was reported by Usuki et al. [1997], who used a functional oligomer (PP-OH) with polar telechelic OH groups as a compatibilizer. In this approach, the PP-OH was firstly intercalated between the layers of organoclay 2C₁₈-MMT, and then PP-OH/2C₁₈ was melt

blend with PP matrix to form an intercalated structure. Since the Toyota research group first reported the successful preparation of PP/clay hybrid composites with the aid of maleic anhydride grafted polypropylene [Kato et al, 1997; Usuki et al. 1997], maleated polyolefins have become one of the most popular compatibilizers used for polyolefin nanocomposites. Kato et al. [1997] reported that the mechanism of how compatibilizers improve intercalation of polymer chain into clay interlayers took two steps. First, chains of compatibilizers intercalate into the silicate layers due to the strong hydrogen bonding between the polar groups of the compatibilizers (i.e. maleic anhydride group) and the oxygen groups of the silicate. The interlayer spacing increases and therefore interaction between layers is weakened. In the second step, chains of the non-polar polymer matrix intercalate into the clay interlayers because of favourable compatibility between the polymer matrix and compatibilizer.

There are two chemical properties of maleic anhydride-grafted polypropylene that affect its effectiveness reported in literatures: maleic anhydride (MA) content and molecular weight [Wang et al. 2004]. A lot of investigations have been put into the effect of maleic anhydride content. Kawasumi et al. [1997] reported that higher maleic anhydride content improved their compatibility with clay, but simultaneously decreased the miscibility of the compatibilizer with the polypropylene matrix and thus lowered the mechanical properties of the final product. Kato et al. [1997] pointed out that a minimal maleic anhydride content should be reached for intercalation to proceed. The effect of molecular weight of compatibilizers was also studied. It was generally agreed that low molecular weight PP oligomers improved the diffusion into clay galleries. [Kawasumi et al. 1997; Hasegawa et al. 1998; Reichert et al. 2000] Wang et al. [2004] found that although low molecular weight compatibilizers led to better clay dispersion, the higher molecular weight ones provided better mechanical properties for the final products. However, there is no clear theory which decouples the effect of maleic anhydride content from molecular weight [Hong et al. 2005]. A compatibilizer with high maleic anhydride content as well as

high molecular weight is certainly welcomed. But unfortunately, with higher maleic anhydride grafted to the polymer backbone, the molecular weight of the polypropylene will considerably decrease by chain scission which occurs simultaneously with bulk grafting [Shi et al. 2001]. Moreover, the amount of MA-PP should be limited due to its negative effect on the thermal stability and mechanical properties of the products [Thompson and Yeung 2006]. In other word, an optimum composition for individual maleated PP incorporated into the Polypropylene/organoclay nanocomposites should be achieved. Too low of a fraction of compatibilizer will not afford enough polar groups for desirable clay dispersion and too high of a fraction of compatibilizer harms the mechanical properties since the physical properties of compatibilizers are usually inferior to the neat polymer matrix.

2.2.3 Structures of PLS nanocomposites

The mixture of polymer matrix and layered silicates does not automatically form a nanocomposite. If the polymers are unable to intercalate into clay layers, a phase-separate composites is formed, whose properties are in the same range as conventional composites. Generally, the structure of PLS nanocomposites is decided by the degree of dispersion of layered silicates. The dispersion mechanism is usually referred to as exfoliation which follows intercalation. An intercalated structure is obtained when a single or more polymer chains diffuse into the interlayer region of clay structure, forming a well ordered multilayer structure of repeating polymeric and inorganic layers. Exfoliation structure forms when the clay layers are completely separated and uniformly dispersed in the polymer matrix. Obviously, exfoliation structure is most desirable since it maximizes the polymer-clay interfacial area and achieves the maximum stress transfer, leading to the most significant improvement in mechanical and physical properties [Alexandre et al. 2000; Pavlidou et al. 2008]. All three structures mentioned above are shown in Figure 2.2.2. However, a complete exfoliation is difficult to achieve, especially for non-polar polymers. Instead, a mixed intercalated-exfoliated structure is mostly obtained.

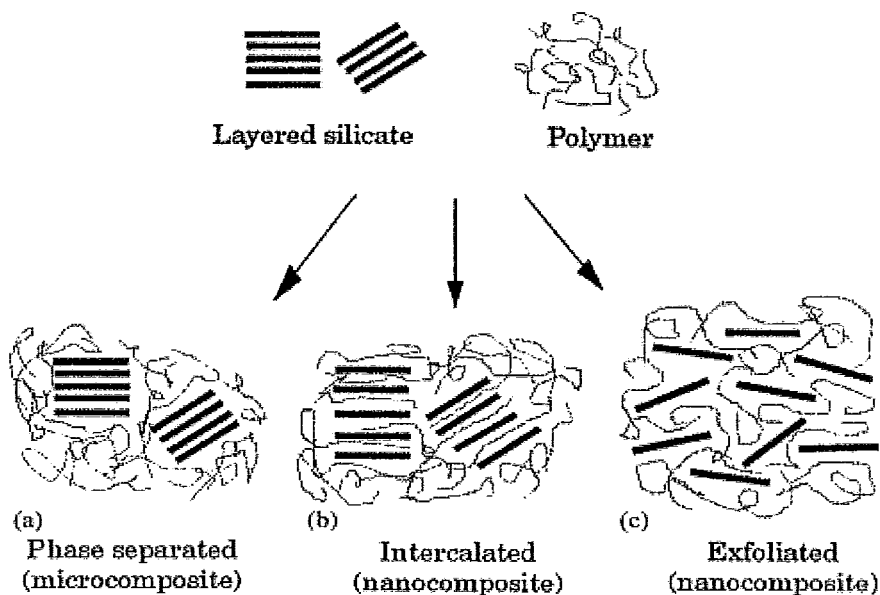


Figure 2.2.2 Structure of polymer/layered silicate nanocomposites

2.3 Preparation of PLS nanocomposites: melt intercalation

There are four principle methods for producing PLS nanocomposites[Alexandre et al, 2000; Ray and Okamoto; Nguyen and Baird, 2006; Pavlidou and Papaspyrides, 2008]: 1) *Template synthesis* (sol-gel technology), by which the clay minerals are synthesized within the polymer matrix, using an aqueous solution containing the polymer. 2) *Intercalation of polymer or prepolymer from solution*, a technique that the layered silicate is exfoliated into individual layers using a solvent where the polymer is soluble. The polymer is then added in the solution and intercalates into clay layers. 3) *In situ intercalative polymerization*, which is the first method used to produce Nylon-6/clay nanocomposite. In this method, the layered silicate is swollen by a liquid monomer or monomer solution and the polymerization reaction takes place between the intercalated layers. 4) *Melt intercalation*, in which the layered silicate is directly blended with the polymer matrix while in its molten state. If the clay layer surface is compatible with the chosen polymer matrix then polymer chains can diffuse into the interlayer spaces and form either an intercalated or exfoliated nanocomposites. Among these four basic

techniques, template synthesis is not suitable for most PLS nanocomposites because of two serious disadvantages: the high temperature needed to synthesize the clay mineral destroys the polymer itself, and growing silicate layers tend to easily aggregate. Methods 2 and 3 usually require large quantities of suitable monomer/solvent or polymer solvent pairs, which lead to a series of economical and environmental issues. Melt intercalation offers a lot of appealing advantages such as no requirement for solvent, ease of processing with conventional compounding devices such as extruders, relatively low cost and environmentally sound, and thus has become the mainstream for preparing PLS nanocomposites in recent years.

The degree of delamination of the silicate platelets and their dispersion in polymer matrix are dependent on the details of the melt intercalation process. Among a variety of shear devices, twin screw extruders were found to be most effective because they provide sufficient amount of shear and resident time [Fornes et al. 2001]. There are two different patterns for intermeshing twin-screw extruders. In the counter-rotating pattern, the screws rotate counter to each other, so that the materials are built up in the junction of the two screws. The disadvantage of this system is that high shear only occurs when the materials passes between the screws, however, total shear is lower than that of co-rotating systems. Whereas, in the co-rotating patterns, the screw rotate in the same direction, which ensure that most of the materials will be subjected to the same shear force when they passes between the screws and the barrel. Moreover, co-rotating systems provide a higher contact time with the extruder barrel, which improves the efficiency of heating. In a word, co-rotating twin screw extruder is more favourable for producing PLS nanocomposites. Dennis et al. [2001] examined the effect of melt processing conditions on the extent of exfoliation in PLS nanocomposites, indicating that increasing shear intensity is not enough to achieve exfoliation. The authors pointed out there are three possible clay delamination pathways: In Pathway 1, clay particles are sheared apart into tactoids or intercalants where high shear intensity is needed. In Pathway 2, polymer chains diffuse into the clay galleries, pushing the end of platelets apart, and expand the

interspace between the clay platelets, where high shear can have a negative influence. In Pathway 3, with more polymers chains entering clay galleries, especially near the edge of the clay interlayers, the platelets tend to peel off of the remain clay (delamination). It appears both Pathways 1 and 2 are included. Thus, residence time in a low/moderate shearing environment is needed to allow polymer chains interact with silicate layers. It is also believed that chemical compatibility between clay and polymer matrix is the most crucial factor in melt intercalation. For well compatible polymer/clay system, only moderate shear intensity is enough to achieve exfoliation structures. While for TPO based nanocomposites, both shear and chemical compatibilization are necessary. Even excess high shear intensity can't help break clay particle smaller than 100 nm thick, unless maleated polypropylene is present as a compatibilizer. Research by Fasulo et al. [2004] showed that clay tends to agglomerate at high processing temperature due to the possible degradation of the intercalant or surfactant between clay layers. Agglomeration is also likely to happen when the feed rate is high because a mass of clay experience relatively high compactive pressure in the extruder.

Obviously, full exfoliation of clay within non-polar polymers like TPO and polypropylene remains a great challenge due to the poor miscibility between the polymer and organoclay. In recent years, some novel strategies have been developed to improve the intercalation or exfoliation, of which adding a small amount of compatibilizers was the most popular. Some other methods, such as the use of ultrasound irradiation [Lim et al. 2003] and electrical fields [Lu et al. 2006], have been reported to improve the exfoliation of the clay only for specific matrices. Interestingly, another novel processing method with the aid of supercritical fluids has gained attention from the plastic industry. [Litchfield et al. 2007; Armstrong et al. 2007; Treece et al. 2006; Horsch et al. 2006; Levit et al. 2005; Zhao et al. 2008; Serhatkulu et al. 2005].

2.4 Supercritical CO₂ in the preparation of PLS nanocomposites

2.4.1 Properties of supercritical CO₂

Above the critical condition, the density of supercritical fluids can be continuously tuned between vapour-like and liquid-like by simply changing the system pressure and/or temperature. Among the various supercritical fluids, supercritical CO₂ (scCO₂) provides a lot of appealing advantages compared to others such as readily accessible critical condition (critical temperature of 31.1°C, critical pressure of 7.40MPa), relatively low cost and environmentally sound [Horsch et al. 2006]. Supercritical CO₂ have other unique properties such as high diffusivity, low viscosity, near-zero surface tension, and ability to solubilise many common polymers [Tomasko et al. 2003]. When above the super-critical state, CO₂ acts like an organic solvent, not only plasticizes a lot of common polymers but also expands the montmorillonite interlayer distances [Litchfield et al. 2007].

2.4.2 Application of supercritical CO₂ in the preparation of nanocomposites

Generally speaking, the use of supercritical CO₂ to reduce the melt viscosity and to delaminate silicate layers is an appealing approach for melt intercalation. The presence of scCO₂ in the polymer phase will increase the inter-chain distance and free volume, and reduce the inter-chain interactions. Thus, scCO₂ leads to significant changes in properties of polymers such as lowering interfacial tension and reduction of viscosity of the polymer melt [Ma et al. 2007]. It was found in the presence of CO₂ that the melt viscosity of polystyrene melt decreased, even with the addition of clay [Tomasko et al, 2003]. A relatively uniform dispersion of sepiolite in PP using supercritical CO₂ was achieved even without the aid of maleated polypropylene as a compatibilizer by Ma et al. [2007], which is contrary to earlier stated theory that a compatibilizer must be involved in melt intercalation for a non-polar polymer. Since scCO₂ is known as a good solvent and carrier agent for maleic anhydride [Galia et al. 2004], the interaction between scCO₂ and maleic anhydride may disturb the natural function of compatibilizers.

Recently, there have been three approaches reported in literature on the preparation of polypropylene/montmorillonite nanocomposites by melt intercalation with the aid of scCO₂. The first is direct injection of scCO₂ into a molten nanocomposite [Garcia-Leiner et al. 2004; Treece et al. 2006]; The second is pretreating the organoclay with the presence of scCO₂ before adding to the melt [Horsch et al. 2006]; The third is injection of clay along with CO₂ together into polymer melt [Nguyen and Baird. 2007; Rodgers et al. 2008]. Treece and Oberhauser [2006] compared the effectiveness of clay dispersion between the conventional twin screw extrusion and a novel single extrusion with the adding of scCO₂. The authors confirmed that a twin screw extruder which provides sufficient shear and intense mixing is more effective for clay dispersion, and they did see the improvement of exfoliation with the aid of scCO₂. The authors suggested that pretreat the clay with scCO₂ prior to the extrusion may better improve clay dispersion and exfoliation. Litchfield et al. [2007] reported injecting the organoclay within a supercritical suspension into a single screw extruder resulted in better dispersion. Horsch et al. [2006] proposed a mechanism of how scCO₂ delaminates silicate layers: First, CO₂ or its mixture with polymers diffuses between the organoclay interlayers under supercritical conditions. This step should take sufficient time to allow polymer chains and CO₂ to fully intercalate. Then, a fast depressurization follows during which the CO₂ dramatically expands and push the interlayers apart. Finally, the polymer chains remain in the interlayers after CO₂ is removed to prevent a reformation of the layered structure.

2.5 Degradation of PLS nanocomposites

Despite the previously mentioned advantages of melt intercalation, polymer degradation may be a considerable issue that shouldn't be overlooked. Since a certain high temperature (around 200°C) is normally needed during melt intercalation, not only the polymer matrix and compatibilizers may degrade but also the organic surfactant of clay may decompose, which can lead to a significant reduction in the mechanical properties of the final products.

Finnigan et al. [2004] prepared a thermoplastic polyurethane/layered silicate nanocomposite both by melt intercalation and by solvent casting. The former method was found to provide a slightly better exfoliation structure but worse mechanical properties due to the degradation of polyurethane and surfactant. The authors believed that the processing temperature (210°C~220°C) was higher than the onset temperature of degradation for the surfactant used in the organoclay Cloisite 30B (~200°C), which led to a reduction of molecular weight for the polyurethane and worse mechanical properties. Davis et al. [2003] reported their PA6/MMT nanocomposites significantly degraded at a processing temperature of 300°C due to hydrolytic peptide scission. Abu-Sharkh et al. [2003] noted that composites containing maleated polypropylene consumed antioxidants more readily thus exhibited lower stability and degraded sooner compared to non-compatibilized systems. Work by Thompson and Yeung [2006] confirmed that maleated compatibilizer promoted the degradation within the nanocomposites, due to presence of its grafted maleic anhydride group as a chain transfer agent; while organoclay were found to have no effect on the thermodegradation.

In conclusion, an optimum processing condition must be carefully achieved to minimize the negative affect by degradation.

CHAPTER 3 DESIGN AND CONSTRUCTION OF CLAY-scCO₂ INJECTION SYSTEM

3.1 Introduction

A key objective of this project was to develop a clay-scCO₂ injector (*clay injector apparatus*) so that the clay could be injected into the compounding process for a nanocomposite while held in suspension with scCO₂. The injection processing was expected to i) minimize gas content in the extruder, ii) maintain a pressurized zone in the extruder at the point of injection, and iii) keep the clay in suspension with the gas from its original discrete state through until it is compounded into the matrix polymer. To arrive at a suitable injector design, a series of characterization tests were conducted to look at particle properties and particle mechanics for both clay materials and polymer compatibilizer which will be highlighted in this chapter.

3.2 Materials

Three organoclays, Cloisite 20A (C20A), SCPX 1137 and SCPX 2934 as well as the original sodium montmorillonite (NaMMT) supplied by Southern Clay Products were chosen for this project. The chemical structures of these clays are summarized in Table 3.2.1. A maleic anhydride grafted (1 wt% MA) polypropylene compatibilizer, Polybond[®] 3200 (PB3200) was supplied by Chemtura Corporation, with a melt flow rate (MFR) of 115 g/10 min (ASTM D1238). This is the most commonly used compatibilizer for polypropylene nanocomposites manufacture. The originally supplied pellets of the PB3200 were ground cryogenically by Ingenia Polymers to better combine with the organoclay. A mixture of 50 wt% of organoclay and 50 wt% of PB3200 was intended to

be operated in the injector later, so the particle mechanics of this mixture needs to be studied.

Table 3.2.1 Organoclays and their properties

Clay	Surfactant type	Surfactant chemical nature	Surfactant MW	Surfactant content (wt%)*
Cloisite 20A	2–C18 chain intercalant	Dimethyldihydrogenated tallow ammonium chloride	574	38.5 ± 0.2
SCPX 1137	1–C18 chain intercalant	Trimethylhydrogenated tallow ammonium chloride	340	26.8 ± 0.2
SCPX 2934	3–C16 chain intercalant	Methyltrihexadecyl ammonium chloride, 100 MER	739	44.2 ± 0.3

* Determined by ashing in a muffle furnace at 600°C for 1 hour, tested by J. Liu.

3.3 Analysis Procedures

3.3.1 Particle size determination for cryogenically ground PB3200 powder

Rotap sieving analysis technique was used to characterize the particle size distribution of PB3200. The particles of PB3200 (200 g) were separated through a set of 7 sieves of mesh size ranging from 1180 µm to 75 µm in order of increasing fineness. The stack of sieves was mechanically agitated for 20 mins. The mass of PB3200 was divided into fractions corresponding to mesh size and the size distribution was obtained.

3.3.2 Bulk density test

The bulk density of the clays, compatibilizer and their 50/50 mixtures was necessary to determine the size of the injector's bore. In this test, a funnel was suspended above a measuring cylinder (101.2 mm in diameter, 116.6 mm in height). The funnel was filled with a sample of clay or compatibilizer particles, and its contents were allowed to freely flow into the measuring cylinder. The excess material on top of the measuring cylinder

was scraped off with a straight edge. The sample and the cylinder were then weighed and the weight / volume (bulk density) was determined.

3.3.3 Angle of repose test

Two methods were utilized to determine the angle of repose, static and dynamic. The difference is that the former test is mostly applicable to hoppers and silos where as the latter one applies better to shear flows. Both methods are described in detail in the follow sections.

3.3.3.1 Static Angle of repose of Free-Flowing Powders

Each sample of clay was dried in a vacuum oven overnight at 80°C to remove moisture before test. In the test, a ring stand with funnel was placed above a sheet of glazed paper on the base plate. The position of the funnel was adjusted so that the height of the funnel nozzle was 3.81cm above the base (according to ASTM C1444-00). A stopper was placed over the funnel nozzle and the clay powder was fed into the funnel until nearly full. The stopper was removed and clay was unceasingly added into the funnel at a rate similar to its discharge rate until the tip of the clay powder cone enters the funnel nozzle. Measure the diameter of the cone in four places. The test was repeated two more times. The angle of repose was calculated as follows:

$$\lambda = \tan^{-1} \left(\frac{2H}{D_A - d} \right)$$

where:

H = height of the cone, 3.81cm

D_A = average of the three test determinations of diameter of the cone

d = internal diameter of the funnel nozzle

λ = angle of repose, in degrees

3.3.3.2 Dynamic angle of repose in Rotating Drum

One third of a 15.2 cm diameter horizontally mounted drum was filled with clay. The drum was rotated at 10 RPM for 1 minute and the whole process in the rotation drum was recorded by digital camera. Digital images were analyzed to find the maximal and minimum leading angles of the clay. Measurement of the two angles from the horizontal plane was done using SigmaScan Pro image analysis software and the average value was reported as the angle of repose.

3.3.4 Cohesive properties

Cohesive properties were measured by a Jenke direct-shear tester. Three samples of clay, each having the same mass (40g), were tested under an applied normal load of 5 kg, 10 kg and 15 kg respectively. Same tests were done on PB3200 and 50:50 C20A/PB3200 mixture, under the applied vertical load of 0 kg, 5 kg and 10 kg since 15kg is not available due to machine limitation.

3.3.5 Capillary Rheology of C20A/PB3200 blend

In the proposed clay-scCO₂ injector, a dry blend of 50wt% C20A and 50wt% of PB3200 will be added and then melting before injected into the twin screw extruder. As it will be necessary to maintain the system above the critical pressure of CO₂ both in the injector and in the injection zone of the extruder, it was necessary to measure the shear viscosity of the mixture in order to estimate the pressure drop through the injector's connection to the twin screw extruder. As the dry blending method produces agglomerates too large for the bore of the capillary die of the rheometer, it was necessary to prepare the mixture first by melt blending in the Haake Rheocord 3000 at temperature 200°C and 50 RPM for 10 minutes, and then grinding it. The measurement was performed using a dual bore

ROSAND capillary rheometer. The viscosity of the blends was measured at 180°C and 200°C.

3.4 Results and discussion

3.4.1 Particle sizes of Polybond 3200

The particle size distribution of PB3200 is shown in Table 3.4.1. It appeared that despite the cryogenic grinding of PB3200, the ductile material maintained a particle size almost 20 times greater than the clay, which usually has a nominal particle size of 20 microns. Despite the difference in particle size, the size difference is not sufficient for segregation of the mixture to occur once uniformly dispersed.

Table 3.4.1 Particle size distribution of PB3200

Particle size (μm)	<300	300 - 500	500 - 850	850 – 1180	> 1180
Frequency (%)	4.90 ± 1.1	13.1 ± 0.3	35.4 ± 2.5	28.4 ± 0.5	18.2 ± 1.8

3.4.2 Bulk density

The bulk density of the four types of clays is summarized in Table 3.4.2. C20A showed the highest bulk density but the differences between the organoclays and original montmorillonite (NaMMT) were not much different. The higher bulk density of polymer compatibilizer and the mixture was related to the larger size of the particles.

Table 3.4.2 Bulk density of clays and compatibilizer

Sample	C20A	SCPX1137	SCPX2934	NaMMT	PB3200	PB3200/C20A
Bulk density (g/cm ³)	0.288 ±0.001	0.283 ±0.001	0.254 ±0.002	0.255 ±0.002	0.334 ±0.001	0.371 ±0.001

3.4.3 Angle of repose

The original intent of the desired CO₂-aided process was to inject the clay alone into the process while maintaining the supercritical state of the gas. In the case of Baird's research group [Litchfield et al. 2007] a high pressure fluidized bed apparatus achieved this goal with the inclusion of ball bearing to mill the clay. The main issue with the proposed system is the enormous amount of gas added to the extrusion system would excessively plasticize the receiving melt stream. The difficulties experienced by Baird necessitating the use of ball bearings in his apparatus are thought to be related to the Geldart classification of these organoclay materials. Geldart [1973] classified particles into four groups based on different particle size and cohesiveness observing their fluidization behaviours. The classification groups are a representation of difficulty for particulate matter to flow. Cloisite 20A and the other organoclay materials are classified as a cohesive class of particles known as Geldart group C powders. Such type of powder is extremely difficult to fluidize and to cause to flow. When exposed to the fluidizing gas (which in our case would be scCO₂), the powders will form crack, channels or even lift as a solid plug because of their strong interparticle forces which generally exceed the force resulting from the action of a moving gas [Chen et al. 2009]. To confirm the group classification of our organoclay powders and determine whether clay powder addition alone was feasible from the processing standpoint, the flowability of the particulate matter had to be evaluated. The angle of repose is a suitable measure for this purpose, with higher angles representing poor flow ability.

The static and dynamic angle of repose of organoclay and original montmorillonite are shown in Table 3.4.3. The natural montmorillonite was included in the comparison to see the effect of the organic coating on the overall cohesive nature of the clays.

Table 3.4.3 Angle of repose for organoclay and original montmorillonite

Sample	C20A	SCPX1137	SCPX2934	NaMMT
Static Angle of repose (°)	51.61 ± 0.41	51.38 ± 0.19	44.59 ± 0.31	51.21 ± 0.43
Dynamic Angle of repose (°)	43.32 ± 0.48	43.13 ± 0.82	39.11 ± 0.89	42.54 ± 0.78

Both static angle and dynamic angle of repose showed that all clays were similar in value, though SCPX 2934 had a slightly lower angle, possibly due to its higher extent of oleophilic coating compared to the others. Note that free flowing powders typically exhibit an angle of repose below 10° and a value greater than 45 degrees indicate a cohesive material. Thus, using the clays alone in an injector apparatus was anticipated to demonstrate great difficulties, and under the highly compactive pressures needs for supercritical CO₂, only serve to create larger aggregates if injected rather than moving towards the goal of finer dispersions in the melt.

The static angle of repose for PB3200 and the 50:50 C20A/PB3200 is shown in Table 3.4.4. The high cohesive nature of C20A dominated the flow-ability of its 50/50 mixture with PB3200. Ultimately, this mixture too was not seen as a viable system to be added in its solid-state from an injector apparatus into an extruder.

Table 3.4.4 Static Angle of repose for PB3200 and its 50/50 mixture with C20A

Sample	C20A	PB3200	C20A/PB3200
Static Angle of repose (°)	51.61 ± 0.41	45.51 ± 0.14	49.96 ± 0.04

3.4.4 Cohesive properties

The angle of repose does not fully describe the cohesive properties of a powder since it is a function of many attributes beyond simply the interfacial properties of the material. In

the case of particle matter under elastic compliance, the state of cohesion is described by the Mohr-Coulomb yield criteria:

$$s = \tan \varphi \cdot \sigma_n + C \quad (1)$$

where:

s is the maximum shear stress, $s = \frac{P_{h(\max)}}{A}$, $P_{h(\max)}$ is the best value of ultimate shear force, and A is the cross-sectional area of shear-box sample, which was 0.00355 m^2 in our case;

σ_n is the nominal normal stress, $\sigma_n = \frac{P_v}{A}$, P_v is the total normal load (which included the top half of shear box and hanger which made a total of 5.94 kg in these tests).

φ is the angle of internal friction and C is the cohesion, both being indicators of the internal state of the bed in regards to flow-ability.

The cohesive properties of all samples are summarized in Table 3.4.5. The resulting values for the angle of internal friction followed the trend of angle of repose: C20A, SCPX1137 and NaMMT demonstrated similar friction angles while SCPX2934 had a smaller result. The cohesion value for the clays, which represent the threshold to yielding, was found to be dependent of the organic surfactant content, increasing with increased surfactants. SCPX2934 exhibited the greatest cohesive behavior followed by C20A then SCPX1137 while NaMMT was found to be cohesionless (i.e. shear stress/normal stress plot passes through the origin). However, the larger internal friction angle for the compatibilizer found in this test in comparison to the neat C20A stands in contrast to the angle of repose measurement. This discrepancy is not uncommon because the angle of repose is a less analytical measure of cohesion, being a complex function of friction, cohesion particle size and particle shape. By the direct shear test it appears that the compatibilizer exhibits lower flow-ability.

Table 3.4.5 Cohesive properties for all particle samples*

Sample	NaMMT	SCPX 1137	SCPX 2934	C20A	PB3200	C20A/PB3200
Angle of friction (°)	39.9	39.1	34.4	39.1	45.9	43.5
Cohesion (kPa)	0	1.72	7.33	2.09	3.97	5.29

*Percentage of error was 4%

3.5 Construction of the clay-injector

Competing technologies for the processing PLS nanocomposites using supercritical CO₂ as an exfoliating aid are, 1) the expansion of clays according to the Manke patents [US6,469,073 and US6,753,360] assigned to Ford Motors, and 2) the fluidized bed apparatus of Dr. Baird [Litchfield et al. 2007; Nguyen and Baird. 2007] assigned to Virginia Tech. The former technique relies upon catastrophic fracture of the clay as a pre-conditioning step and then using the prepared clay in the same manner as normal clays in the compounding of a PLS nanocomposite; the latter technique adds clay to a single screw extruder from a fluidized bed. There are serious concerns of excessive gas content in the melt during mixing in the extruder; however, at this point in time there have been no serious way to assess the method. It is known from released information on the technique that a gas/clay mixture is being added to a low pressure zone and therefore is not being kept as a suspension. However, the proposed injector in our project was expected to maintain the clay in suspension with gas during the whole compounding processing. Moreover, the injector was desired to reduce the volume of the scCO₂ being used in the whole system, due to limitation on the volume that can be generated by the syringe pump, poor mixing in the extruder, and the complexity of devolatilizing a heavily gas laden melt at the end of the extruder. Finally, this injector should be inexpensive and represent technologies familiar to polymer processors so that it can be quickly implemented for commercialization.

Considering that the oragnoclays are Geldart C powders, which means that their cohesive properties limit flow without extreme fluidization and they will compact into hard agglomerates under pressure, gear pumps should not be considered for use due to the agglomeration issue. Since clays were very difficult to inject alone, we examined the possibility to inject clay/compatibilizer mixture together into the extruder, but we found that this mixture is still too cohesive to directly inject into the extruder in its solid state. Thus, the injector should be sufficiently heated to melt the mixture before injecting. Based on our previous results, C20A was found to show the best beneficial change in interlayer spacing in scCO₂ condition; PB3200, a compatibilizer with moderate molecular weight, was found intercalate well with the presence of CO₂ and offer greater mechanical property than low molecular weight ones. Therefore, a dry blend of C20A and PB3200 was proposed to be added and then melting before injection into the twin screw extruder.

The injector was designed based on the concept of a ram extruder. The design was to be considered a preliminary lab version, for short term runs in the order of 20-30 minutes in duration. The extrusion line was designed to run at 5 kg/h. The chamber was sized to hold clay and polymer powder with a bulk density of 370 kg/m³. Based on the properties of selected clay material and compatibilizer, the dimension of the injector was determined as shown in Table 3.5.1 and the design was shown in Figure 3.5.1.

Table 3.5.1 Dimension of the injector

	Cylinder	Shut-off Nozzle	Twin Screw Adapter
Inner Diameter (mm)	63.5	12.7	12.7
Length (mm)	190.5	139.7	101.6

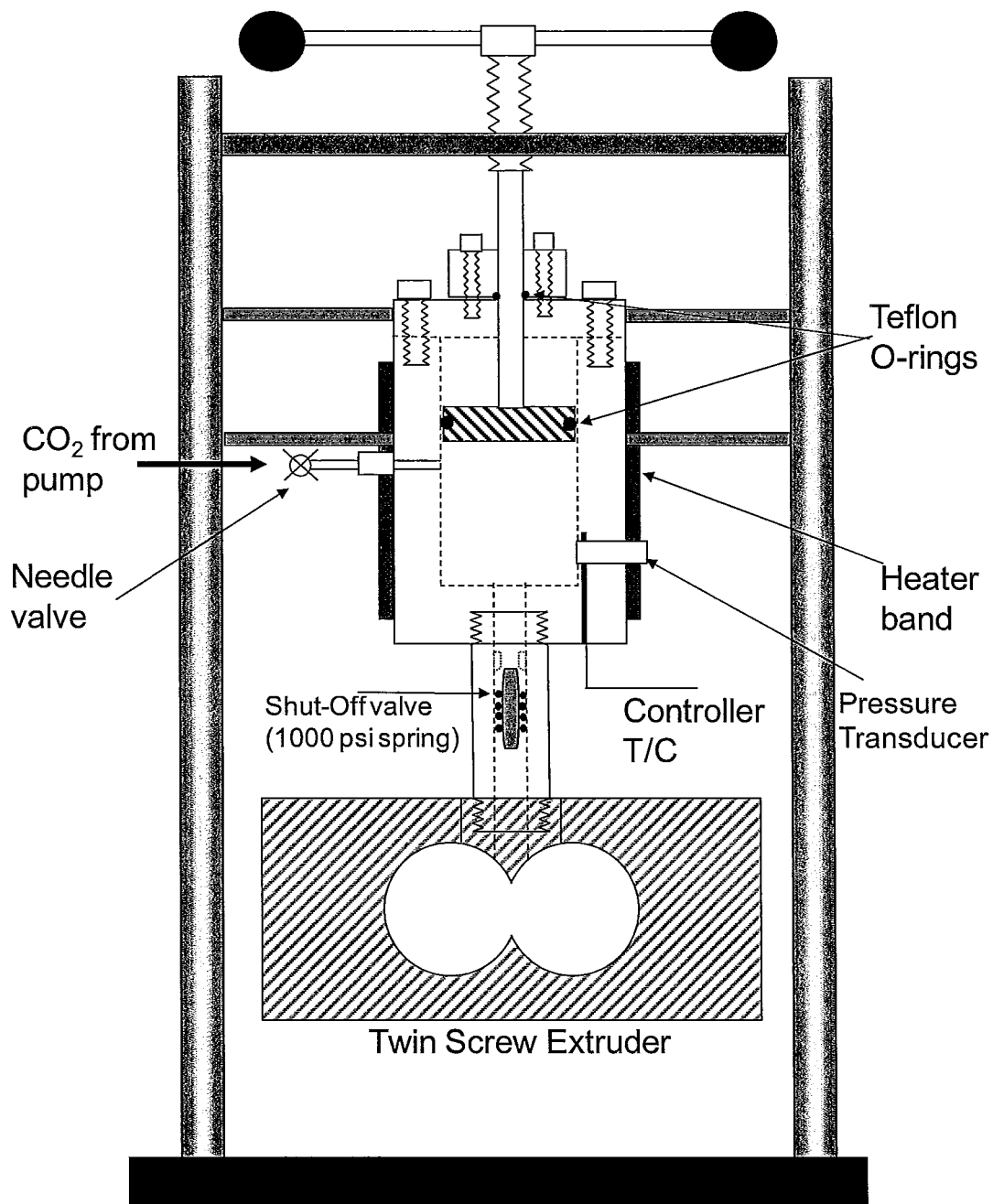


Figure 3.5.1 Drawing of proposed injector over the twin screw extruder

It was necessary to measure the shear viscosity of the mixture in order to estimate the pressure drop through the injector's connection to the twin screw extruder. The viscosity curve for blend is shown in Figure 3.5.2. According to the power law model, the fitted expression for the viscosity curve at 200°C was:

$$\eta(\dot{\gamma}) = 14154 \cdot \dot{\gamma}^{-0.82}$$

The large negative power law index of -0.82 indicates significant shear thinning attributes by the mixture once molten. Fortunately, the designed injector will require only minimal force to add the mixture to the compounding process. The pressure drop for the current configuration of injector is calculated as follows:

$$\Delta P = \frac{2L}{R} \times \tau_w$$

where: L is the total length of shut-off nozzle and the twin screw adapter, $L = 0.2413\text{m}$

Q is the flow rate of the C20A/PB3200 mixture according to a set mass flow rate of TPO at 5kg/h , $Q = 1.13 \times 10^{-7} \text{ m}^3 / \text{s}$

R is the radius of the shut-off nozzle, $R = 6.35 \text{ mm}$

$$\tau_w \text{ is the shear stress at the wall, } \tau_w = m' \left(\frac{4Q}{\pi R^3} \right)^n = 14640 \text{ Pa}$$

Thus, the pressure drop ΔP is estimated 1.1 MPa. This value is used to adjust the pressure in the injector.

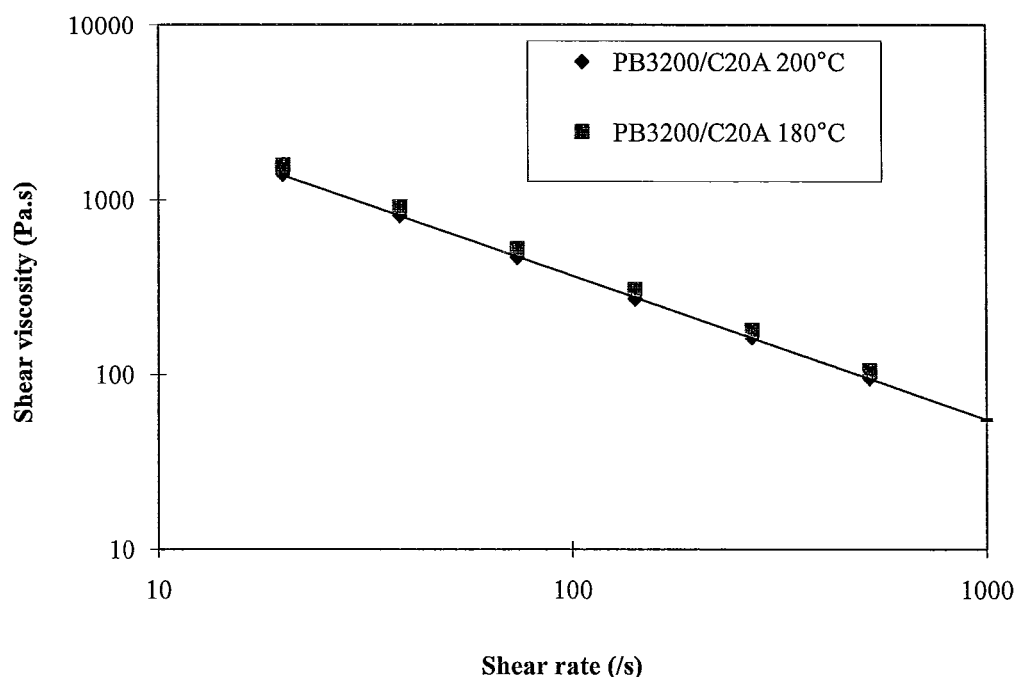


Figure 3.5.2 Shear viscosity curve for C20A/PB3200 blend

The injector underwent several design changes during numerous experimental trails. The apparatus was finally mounted horizontally to be more safely handled. In use, the top plate along with the piston will be removed and a mixture of clay and compatibilizer (~50:50) added to the chamber at the start of the experiment. A well mixed clay-compatibilizer powder mixture should minimize agglomeration during compaction. The top plate and piston would be put back into place, and the system pre-consolidated so that solids will not melt near the gas inlet later. The gas line can then be connected to the syringe pump and the injected would be charged with gas until reaching supercritical pressure. Once the pressure was ready, the injector can be heated up to 200°C. Heating of the device was done by two 1000 W ceramic heater bands and used the auxiliary connectors of the twin screw extruder to supply power and control its temperature. The heating of the connector pipes used flexible silicone heating tape. While heating the syringe pump can be used to regulate the pressure inside the injector. The gas inlet was

positioned close to the fully retracted piston so that i) polymer melt can not enter the gas line during operation and ii) gas can be injected on the backside of the piston to assist its displacement should the need arise. Once ready to run, the twin screw extruder was started up first, building up desired pressure in the injection zone. The clay/compatibilizer suspension was then injected by the piston, which was displaced manual by using a screw & wheel.

There were two major problems led by the natural design of this injector. Firstly, owing to the large plug of polymer/clay in the 6.35cm diameter x 19cm long bore of the injector, it was readily recognized that reducing the viscosity of the material to an extrudable state would be difficult due to the low thermal conductivity of compatibilizer and clay. To assist in minimizing the issues of heat transfer, the entire injector was jacketed with high-temperature glass fiber insulation. The transient heat profile was monitored by inserting a melt thermocouple through the exit pipe into the injector. Unfortunately, we found that in order to get the core close to a temperature close to a reasonable melt temperature of 180°C, polymer at the outer walls would be held at temperature around 300°C, which was close to its degradation temperature. Secondly, all shut-off valves we tried could not limit gas and polymer from escaping the injector at evaluated temperature (>200°C) and evaluated pressure (>8.3MPa). Grafoil and graphite-impregnated Teflon seals have been found to rapidly fail under such conditions. Teflon alone has performed consistently but the gas must not be released too quickly else swelling occurring leading to substantial gas leakage in following uses. We finally adopted an elbow tube which was filled with solid low density polyethylene (LDPE) plug to connect the injector and twin extruder. In use, when the injector was being heated, this tube was cooled by water so the polymer remained frozen and was able to maintain the pressure in injector; when the injection experiment were about to start, the tube was heated by flexible heating tape to melt the polymer. Since LDPE has a low melt point around 145°C, it only took 25 minutes to melt and then polymer-clay mixture could be injected into the extruder.

CHAPTER 4 PROCESSING OF TPO NANOCOMPOSITES UNDER SUPERCRITICAL CO₂ CONDITION

4.1 Experimental

4.1.1 Materials

A medium-to-high flow TPO (13 MFR, according to ASTM D1238) supplied by LyondellBasell was selected for the polymer matrix. Pellets of the TPO material were used as supplied without any further treatment. Cloisite 20A (C20A), the organically modified montmorillonite, was supplied by Southern Clay Products. The maleated polypropylene (MA-PP), Polybond[®] 3200 (PB3200) from Chemtura Corporation was selected as the compatibilizer. This compatibilizer has moderate molecular weight to minimize any negative reduction of viscosity for the compounded melt or dramatically reduce mechanical properties of the end product. The maleated polypropylene had also demonstrated plasticization in supercritical CO₂ condition sufficient to aid intercalation [Liu et al, 2009]. The originally supplied pellets of the MA-PP were ground cryogenically into powder to better combine with the organoclay. Carbon dioxide gas (> 99.5 mole % purity) and nitrogen gas (100 mole % purity) were supplied by Air Liquid Canada Inc.

The formulation of materials examined in this thesis consisted of weight fractions 0.90:0.05:0.05 for TPO:PB3200 (Polybond 3200 MA-PP):clay (Cloisite 20A). There were two different states of added clay. The species referred to as **C20A** was the as-supplied Cloisite 20A from Southern Clay Products. The species referred to as **s-C20A** was preconditioned with supercritical carbon dioxide (scCO₂). The C20A clay was placed in a high pressure vessel (HPV), annealed in supercritical CO₂ condition at 9.7MPa and 200°C for 3 hours, followed by rapid depressurized with a release rate 4.8MPa/s.

4.1.2 Apparatus

A high pressure vessel (HPV) was built to pretreat organoclay with scCO_2 . Temperature and pressure in the vessel were regulated by a temperature controller and a high pressure syringe pump (ISCO Model 260D). The setup of the HPV is shown in Figure 4.1.1.

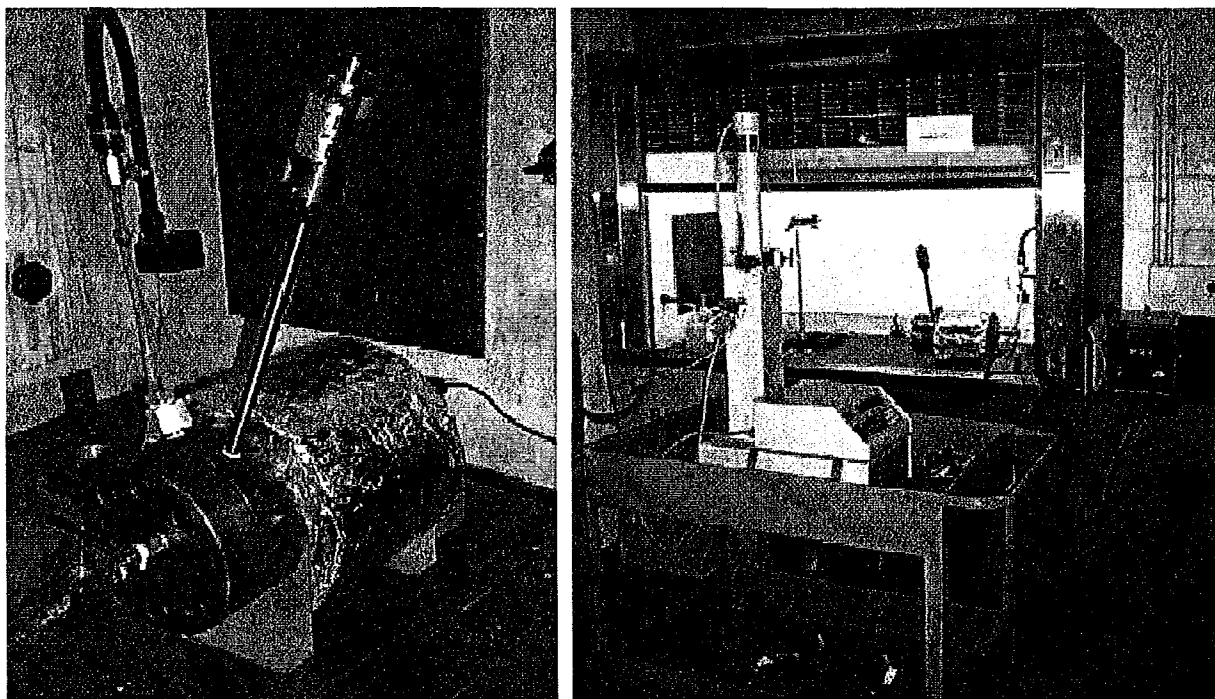


Figure 4.1.1 High Pressure Batch Vessel (HPBV, left) together with syringe pump (right)

A clay- scCO_2 injector (*clay injector*) was designed and built so that the clay could be injected into the extruder while held in suspension with scCO_2 . Details of this injector have been introduced in Chapter 3.

A ZSE-HP 27mm 40 L/D Leistritz co-rotating twin screw extruder (TSE) with a maximum screw speed of 600 RPM was used to melt compound the nanocomposites. Three different screw designs were tested, monitored by pressure transducers over the injection point, upstream melt seal, and first downstream mixing zone. The final compounding screw (shown in Figure 4.1.2) represents the optimal for mixing intensity as

well as melt pressure generation – the latter being the critical parameter for consideration. The TPO pellets were to be added at the feed opening, melted and rapidly pressurized to build a melt seal in order to prevent gas loss out the opening. Downstream from the first melt seal, a low pressure zone was created for the *direct CO₂ injection method*, in order to prevent melt pushing backwards along the gas injection stem. In the following barrel zone can be found the first distributive mixing section (Zone 6) to improve homogeneous dispersion of the gas in the polymer melt. This screw was also used for the *clay injector system* which fed above Zone 4. Subsequent conveying and mixing zones continued to provide shear for exfoliation of the clays, though the gas will only remain in phase with the polymer in the fully filled mixing regions and due to energy dissipation was unlikely to remain in its supercritical state. The final zone before the die was a devolatilization zone where the melt and gas are allowed to separate.

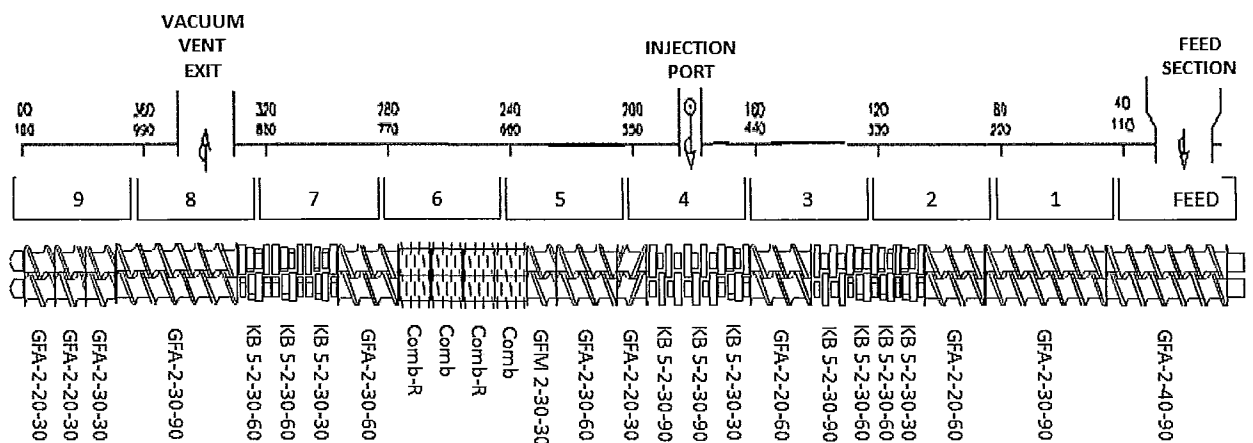


Figure 4.1.2 Screw design and barrel configuration for compounding

A Davis Standard 50mm 28:1 L/D single screw extruder (SSE) was also used in the experiment. A 12 mm dia. valved die adaptor was used to regulate the die pressure. The injector was located approximately 2/3 of the distance down the barrel length and barrel

temperatures of 200°C for all three zones. A moderate work DSB-I barrier screw was used and screw speed was set 20 RPM.

4.1.3 Extrusion experiments

Three methods for preparing TPO nanocomposites were discussed in this thesis: **Method 1**, in which the gas was directly injected in to the extruder similar to conventional foaming practices (*Direct gas injection method*); **Method 2**: the clay/CO₂ suspension was injected into a twin screw extruder at high pumping pressure (*TSE clay-injection method*); **Method 3**: the clay/CO₂ suspension was injected into a single screw extruder at high pumping pressure (*SSE clay-injection method*). Details of three methods are introduced as follows:

Method 1:

The TPO nanocomposites were prepared in a two-stage process. In the first pass, the clay and TPO were added by two separate gravimetric feeder into the feed opening of the extruder. The clay (s-C20A) was fed into the extruder at a mass flow rate of 1 kg/h and TPO was added simultaneously at 18kg/h. The speed of the screws is 120RPM. This stage dispersed the clay thoroughly within the polymer matrix but without the clay exfoliation. It is generally agreed that without the addition of the maleated polypropylene compatibilizer, no exfoliation will occur for a polyolefin material⁹ [Ratnayake et al. 2006]. Since our primary interest is to see if clay exfoliation is enhanced by the addition of scCO₂, it was undesirable to achieve any delamination during this first pass while the gas was not present. The barrel temperature profile during first-pass processing was shown in Table 4.1.1.

Table 4.1.1 Barrel temperature profile during Stage 1 processing

Barrel Zone	1	2	3	4	5	6	7	8	9
Temperature (°C)	120	163	170	170	170	170	190	200	200

In the second pass, it was necessary to bring down the barrel temperatures to 105°C around the mixing zone in order to reach a pressure greater than the critical pressure of CO₂, i.e. reached a pressure of 8.3MPa. This temperature is 65°C below the melt crystallization temperature of the base polypropylene matrix in the TPO, and would be a solid were it not for the mechanical energy supplied by the TSE. The clay filled TPOs, which were collected in the first-pass, were tumble-blended with PB3200. The feed rate was slowed to 6kg/h in order to lengthen the time the gas in the syringe pump would last. TPO/C20A was first run through as a purge material and once the process was stable the barrel temperatures were gradually decreased; it was not possible to start up the machine at the 105°C barrel zone setting so the process had to be slowly lower from 170°C over a 15 minute period. The final barrel temperature in this stage was shown in Table 4.1.2 and the extruder speed was set to 50 RPM since higher screw speed exceeded the torque limit of the machine and was not necessarily desirable for maintaining gas and melt in a single phase. With stable operation achieved at the final barrel profile, the material containing compatibilizers in the gravimetric feeder was switched without disturbing the conditions in the extruder and the scCO₂ was added at the injector stem located in Zone 4.

Table 4.1.2 Barrel temperature profile during Stage 2 processing

Barrel Zone	1	2	3	4	5	6	7	8	9
Temperature (°C)	120	130	105	105	105	145	190	200	200

A selection of samples were prepared from the two materials based on whether they were collected during the first or second stage of the procedure and depending on the concentration of CO₂ added into the process. The samples were listed in Table 4.1.3.

Table 4.1.3 Sample list of prepared materials by Method 1

Sample	TPO wt%	C20A wt%	s-C20A wt%	PB3200 wt%	CO ₂ % (w/w formulation)
1	90	5		5	0
2	90	5		5	1.5
3	90	5		5	4.3
4	94.7		5.3		0
5	94.7		5.3		4.5
6	90		5	5	0
7	90		5	5	2.2
8	90		5	5	4.6

Method 2:

In this method, C20A and PB3200 were injected into extruder in a CO₂ suspension or N₂ blanket. The powdered mixture for injection was comprised of 130g PB3200 and 130g C20A which was tumble-blended and then packed in the injector. The injector was heated for 80 minutes with a set wall temperature of 300°C in order to bring the core temperature of the injector up to 180°C. The polymer in the tubing connecting the injector with the extruder was kept solidified by a cooling jacket during this heating stage in order to completely maintain the gas with the clay. When the trial was ready to progress and TPO had pressurized Zone 4, the polymer plug in the tubing was melted with heating tape. The injector was located at Zone 4 for all trials in this method. (Note: the injector was also

tried at Zone 9 in place of the vent but less melt pressure found than at Zone 4 and therefore the location was not pursued.)

Different conditions were tested in these trials. Samples 9 and 10 were prepared with the injector under a nitrogen atmosphere at 4.13 MPa. The nitrogen was used in order to minimize the negative effect of polymer degradation. Sample 11 was prepared with the injector under a sub-critical CO₂ atmosphere (4.13 MPa CO₂). The barrel temperature profile for Samples 8-11 was the same as that of first-pass in Method 1, shown in Table 4.1.1. Sample 12 was the closest trial reaching the goal of a supercritical state for the gas from the injector into the mixing zone of the extruder. The clay/PB3200 mixture was annealed in scCO₂ condition (8.3 MPa) for 80min, and then could be injected in the extruder at 5.86 MPa (sub-critical). The barrel temperature for Sample 12 was set as in Table 4.1.4.

Though reiterated later, the reader will note that pressures rarely reached the supercritical state for CO₂ once in the extruder due to the low viscosity of the TPO. The extruder had to be operated at potential harmful conditions in respect to the machine in order to achieve a high pressure and hence data at the desired state was limited.

Unlike Method 1, the same procedure for lowering the barrel temperature to build up critical melt pressure for the received CO₂ could not be replicated with the injector due to an issue with plugging. We found it necessary to maintain the temperature of the injector zone (Zone #4) above the melt point of TPO, otherwise polymers in the tapped hole of the barrel where the tubing from the injector connects, would freeze thus blocking the pathway for clay and PB3200; no mechanical energy from the motor affected the polymer in this region and it was beyond the heating capacity of the heating tape wrapped around the tubing. (Note: it was for this reason that a higher viscosity polymer, 1 MFR isotactic

polypropylene, tried could not be used in place of the TPO to help build up pressure in this zone.) A lower screw speed of 50RPM was used in some cases to build up pressure, otherwise a speed of 120 RPM was used. But even though, the high temperature in injection portion prevented reaching a critical pressure. All samples prepared in this method are listed in Table 4.1.5.

Table 4.1.4 Barrel temperature profile for Sample 12

Barrel Zone	1	2	3	4	5	6	7	8	9
Temperature (°C)	120	130	105	170	105	120	190	200	200

Table 4.1.5 Samples prepared by Method 2

Sample	Gas environment	Annealing pressure MPa	Injecting pressure MPa	Screw speed RPM
9	N ₂	4.1	4.1	50
10	N ₂	4.1	4.1	120
11	CO ₂	4.1	4.1	120
12	CO ₂	8.3	5.9	50

Method 3:

Two major issues were encountered in Method 2. Firstly, the TPO resin was found to be unsuitable for generating high pressure in the twin screw extruder due to its low viscosity. Alternatively, a single screw extruder may not afford same sufficient shear force as twin screw extruder but higher pumping pressures are readily achieved, particularly with a valved die adapter. The clay-PB3200 mixture could be injected into a high pressure zone and CO₂ could be maintained above supercritical pressure both in the injector and in the extruder. Secondly, the high set-point wall temperature of the injector

(300°C) may have led to significant thermo-oxidative degradation of the compatibilizer. Therefore, a newly conceived two-stage heating profile was used in this method. The injector was firstly heated to 100°C for 1h (well below the melting range of the PB3200 or possible degradation temperature of the surfactant), and then the wall temperature was set at 220°C and heat about 40 minutes until the inner temperature reach at least 180°C. The pass through the single screw extruder made the appropriate nanocomposite at the same ratio of TPO, clay and PB3200 as stated for the other two methods. Some material from each run was subsequently passed through the twin screw extruder to, 1) get rid of any foams, 2) improve the extent of shear delamination now in the absence of CO₂ and its plasticizing effect on the polymer matrix, and 3) balance the clay content in each sample. The TSE operated at a feed rate of 6 kg/h and screw speed of 50 RPM, and used the barrel profile stated in Table 4.1.1. Samples 13-16 prepared by the single screw extruder are listed as follows. All these samples went through the twin screw extruder, and sample 17-20 were also collected.

Table 4.1.6 Samples prepared by single screw extruder

Sample	Gas environment	Annealing pressure MPa	Injecting pressure MPa	Die pressure MPa
13	N ₂	4.1	4.1	4.5
14	CO ₂	4.1	4.1	4.5
15	CO ₂	8.3	5.5	9
16	CO ₂	8.3	6.9	9

4.1.4 Clay content

The clay content for each nanocomposite was determined by the burn-off technique in a muffle oven at 600°C for 1 hour. The reported clay content is an average of three samples. The values reported here include the content of organic surfactant (noted in Chapter 3).

the presence of supercritical CO₂. It indicated that order stacking remaining in the clay interlayers. While this shoulder peak significantly weakened for those nanocomposites based on s-C20A clays, which demonstrated a more effective intercalation. From literature [Thompson et al, 2009], we know that the rapid depressurization in pretreating organoclay results in a porous clay particle, which in the case of s-C20A made it more susceptible to applied forces whether by intercalation under scCO₂ or by delamination during mixing. It appears that annealing the clay in scCO₂ solvent followed by a rapid depressurization is an effective method for polymer intercalation over direct use of as-supplied organoclay. However, these diffraction curves show no evidence that directly injection of scCO₂ in the compounding process further aided exfoliation.

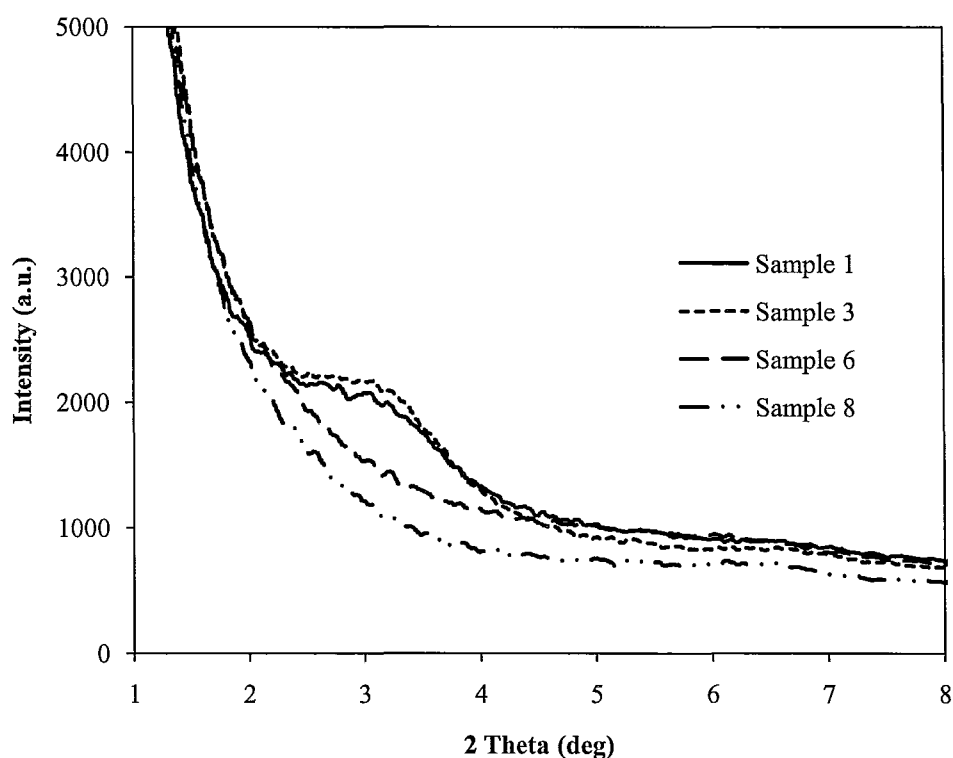


Figure 4.2.2 XRD patterns of nanocomposites filled with C20A and s-C20A

Figure 4.2.3 showed the compatibilizer when the pretreated clay was used in the nanocomposites for Method 1. The shoulder peak shifted to lower 2θ angle with the

presence of supercritical CO_2 , indicating a better intercalation of clay. For nanocomposites containing PB3200, their XRD patterns look similar, no distinct diffraction peak can be observed, indicating the clay stacks dispersed well in both products. The lack of PB3200 yet good exfoliation is a significant advancement for nanocomposites.

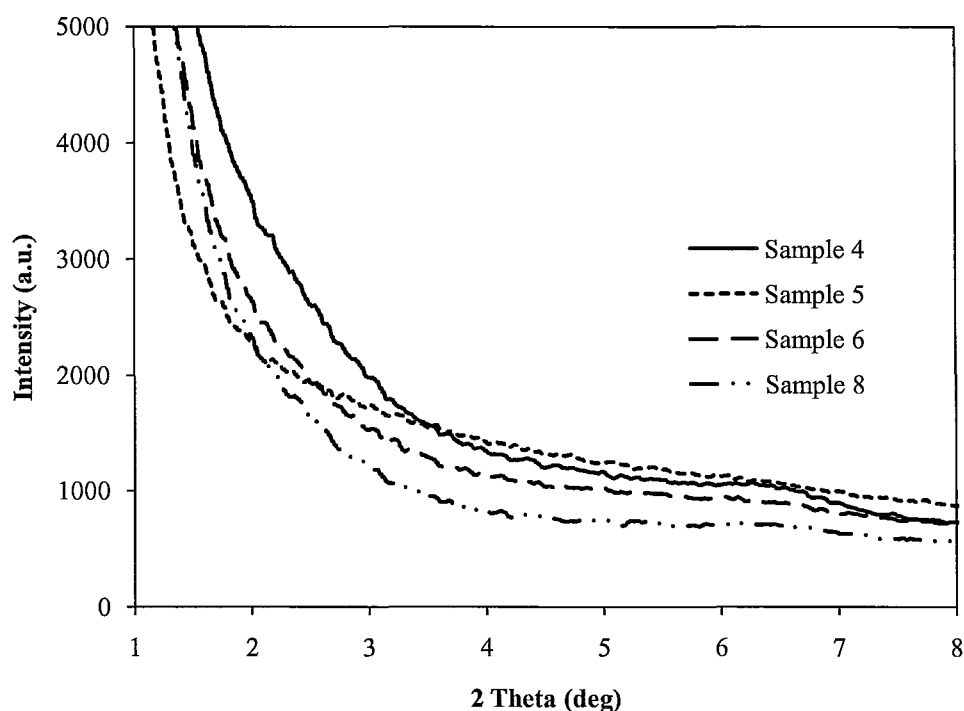


Figure 4.2.3 XRD patterns for TPO nanocomposites based on s-C20A

Figure 4.2.4 shows the XRD patterns for TPO nanocomposites prepared by Method 2 as well as two samples of the 50:50 C20A/PB3200 mixtures taken directly out of the injector after annealed in the gas for 80 min. All samples shown appeared to possess the same diffraction pattern. The main diffraction peak of C20A (referring to the peak in the region of $2\theta = 3-5^\circ$) was almost completely indiscernible from the baseline. A small secondary peak ($2\theta = 6-7^\circ$) was observed for all samples including the C20A/PB3200 mixture. This secondary peak could be attributed to the increasing chain mobility of a monolayer surfactant due to the plasticizing effect by CO_2 . This conformation would only occur

between the interlayers containing low concentration of surfactant [Thompson et al. 2007]. Alternatively, the peak could correspond to galleries in the clay which collapsed due to degradation of the surfactant before the compatibilizer could intercalate. The remaining peak in the TPO nanocomposites suggest the shear forces within the twin screw extruder might not be sufficient to further clay exfoliation. All nanocomposites were compounded at a subcritical pressure in the extruder and they exhibited quite similar XRD diffraction patterns, with no effect by CO₂ was found. The prolonged annealing stage in the injector was sufficient to cause major disruption to the clay structure.

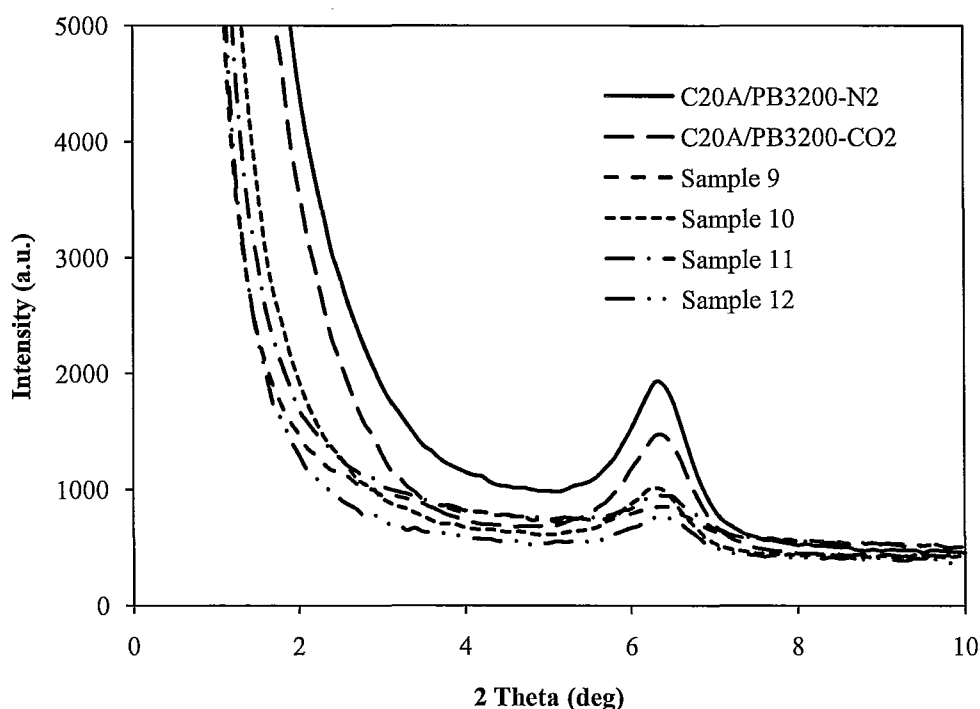


Figure 4.2.4 XRD patterns for nanocomposites prepared by Method 2

XRD patterns for nanocomposites prepared by Method 3 are shown in Figures 4.2.5 ~ Figure 4.2.7. In Figure 4.2.5, a comparison between the CO₂ and nitrogen conditions showed an evident influence of CO₂ on the crystal structure of the clay. For nanocomposites compounded in a nitrogen environment, a shoulder peak lies in the range of 2 θ ~ 3 $^{\circ}$, which indicate that many galleries of the clay did not experience intercalation.

While for all the samples prepared in CO₂ condition, this diffraction peak was broadened and less intense, which indicates the CO₂ was beneficial in intercalation for these trials. However, pressure effect of CO₂ on the clay structure showed negligible differences in the XRD patterns. The diffraction patterns bear close semblance to those found with the pretreated clay (s-C20A) earlier.

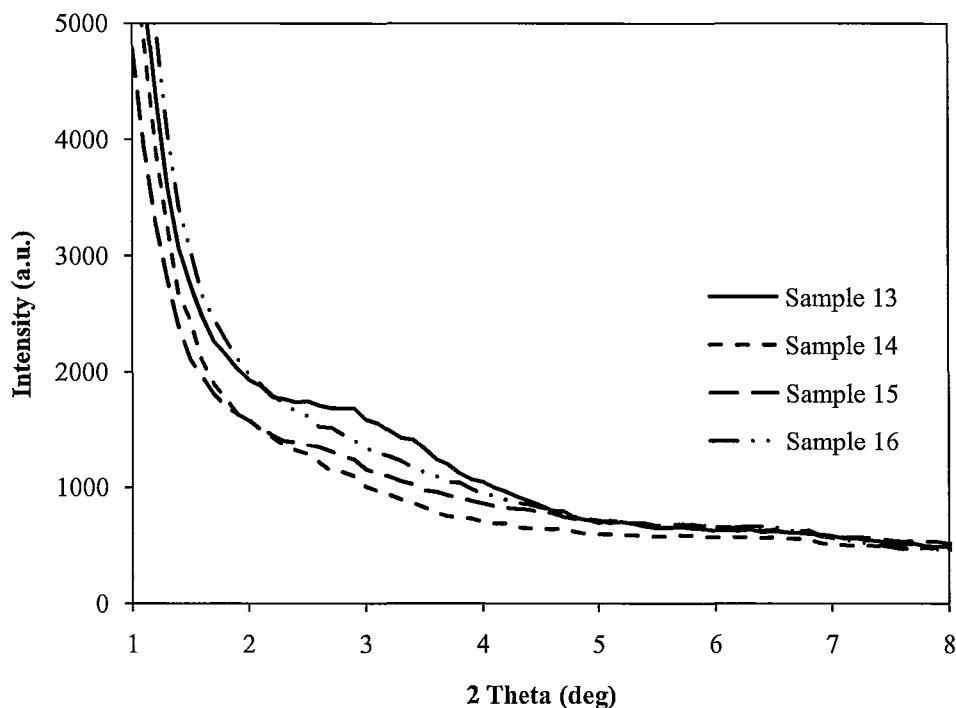


Figure 4.2.5 XRD patterns for nanocomposites from single screw extruder in Method 3

XRD patterns for those samples processed in the twin screw extrusion after the single screw extruder are shown in Figure 4.2.6, in which a pressure dependent trend was found. TPO nanocomposites (Sample 17 and 18) that were prepared under low pressure conditions had an almost identical diffraction pattern for both nitrogen and carbon dioxide case, with a small secondary peak in the diffractograms. While the sample prepared at highest pressure showed the best intercalation, with no diffraction peak visible.

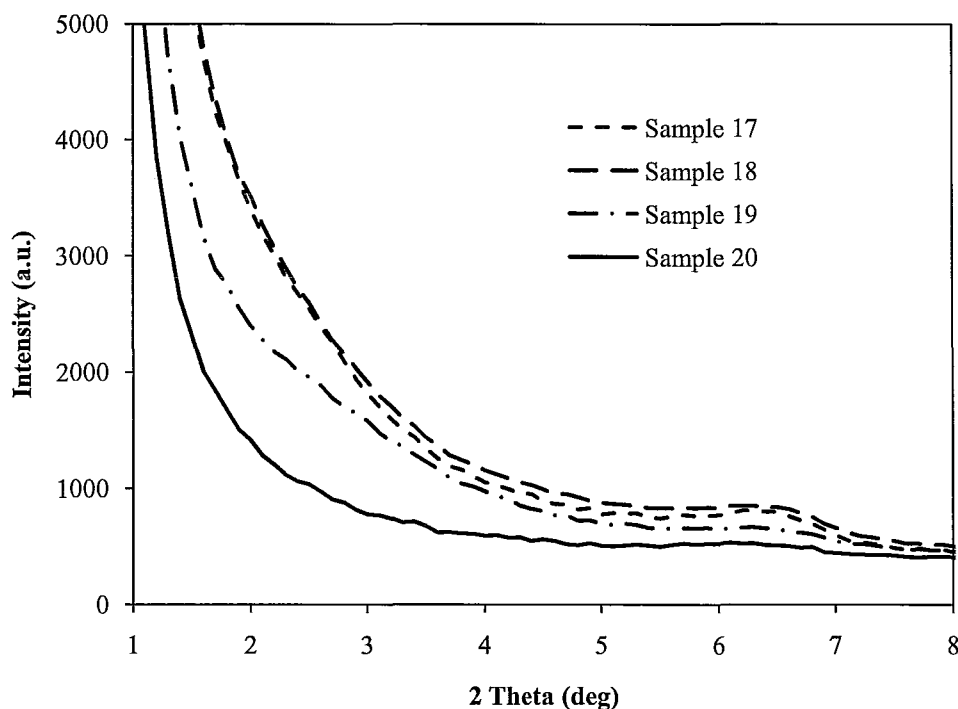


Figure 4.2.6 XRD patterns for nanocomposites by twin screw extrusion in Method 3

The XRD patterns for TPO nanocomposites prepared with the aid of CO_2 by the three different methods are summarized in Figure 4.2.7. It appears that two strategies, 1) pretreating clay prior to extrusion, and 2) injecting clay/ CO_2 as a suspension into the polymer melt and with sufficient shear force applied (by removing the presence of CO_2), both lead to better clay intercalation/exfoliation. The other samples all had distinct diffraction peaks, indicating ordered stacking still remained in the clay interlayers.

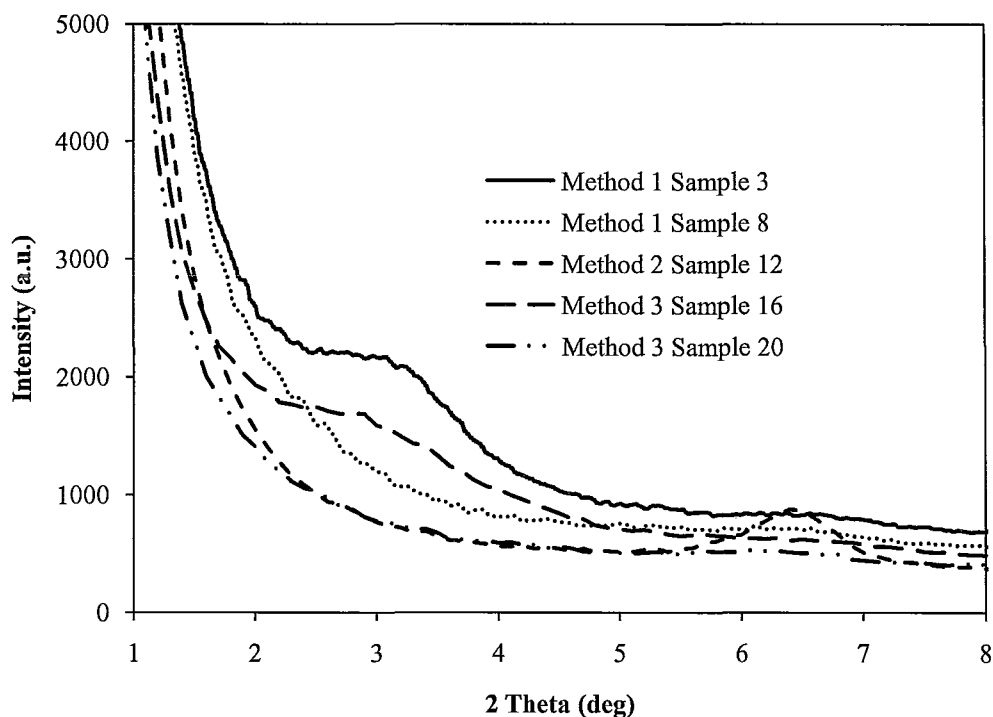
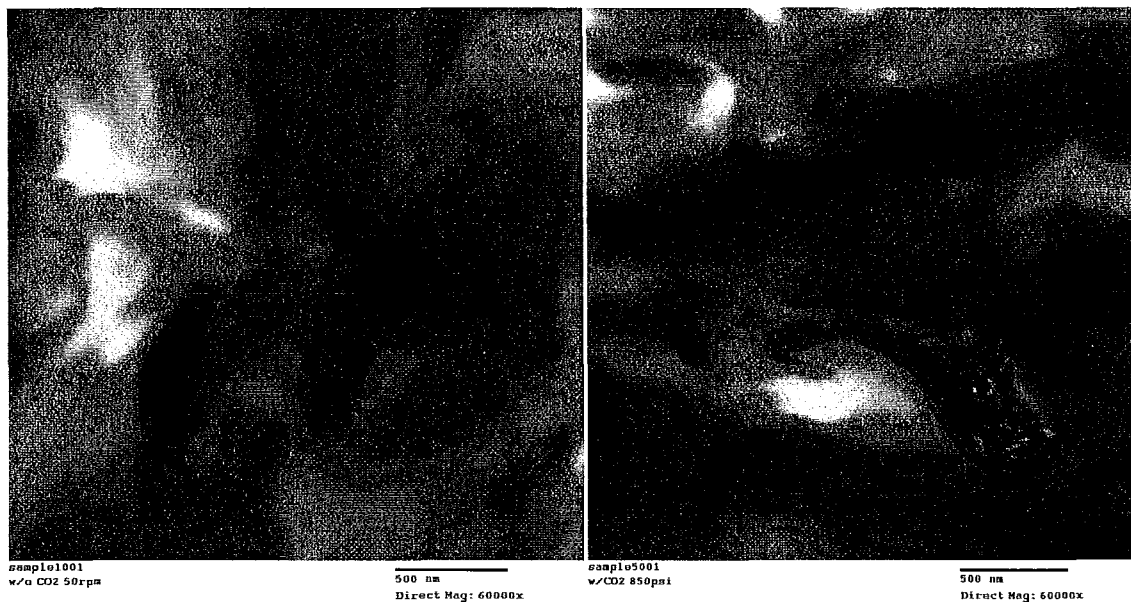


Figure 4.2.7 Summary of XRD patterns for samples prepared by three methods

4.2.3 TEM Analysis

Although XRD is a conventional method for determining the interlayer spacing of layered silicates and the intercalated nanocomposites, it is hard to distinguish the spatial distribution related to its extent of exfoliation. To aid our understanding of the distribution of the clay, TEM analysis was involved.

The TEM micrographs for all nanocomposites can be easily divided into two groups. **Group One** included nanocomposites prepared by Method 2 and those experiencing only first-pass with single screw extrusion in Method 3, in which little dispersion was observed, with most clay layers remaining organized though not necessarily stacked anymore in the polymer matrix. The TEM micrographs of these nanocomposites are shown in Figure 4.2.8.



(a)

(b)



(c)

(d)

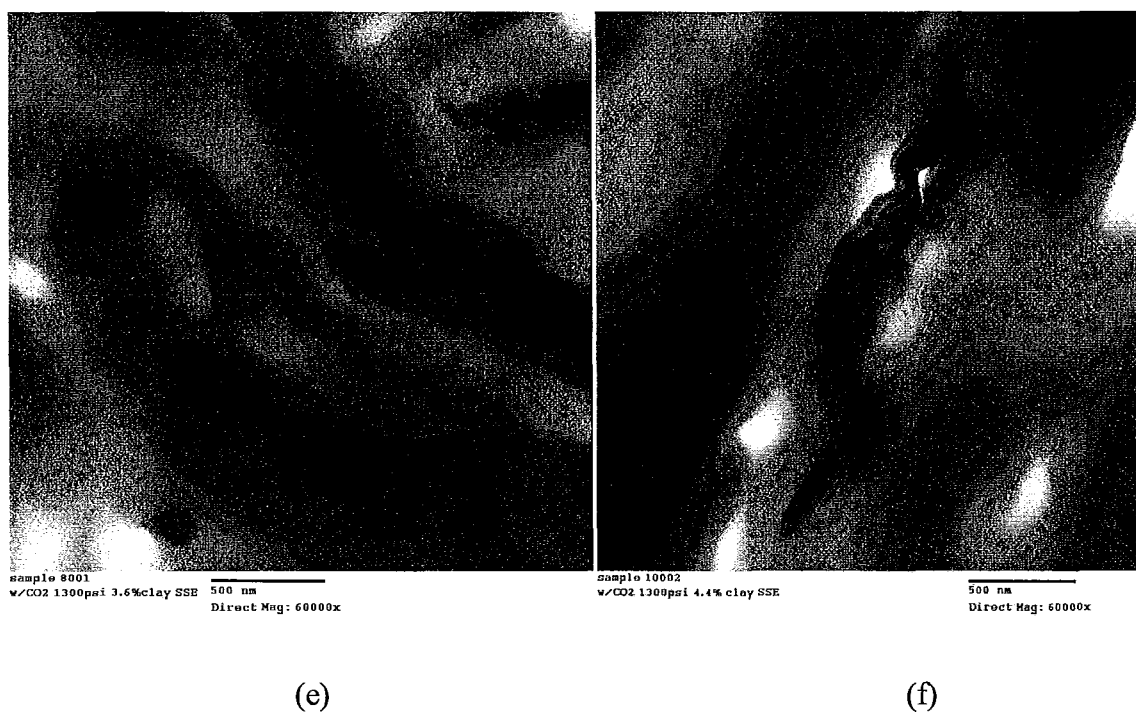


Figure 4.2.8 TEM micrographs for nanocomposites (a) Method 2, Sample 13 (b) Method 2, Sample 16 (c) Method 3, Sample 17 (d) Method 3, Sample 18 (e) Method 3, Sample 19 (f) Method 3, Sample 20

Figure 4.2.8 shows that for these nanocomposites, clay platelets lost their ordered crystalline structure and became disordered with many platelets no longer parallel, which refers to an intercalated disorderd arrangement. The TEM results correspond to the XRD patterns in which no distinct diffraction peaks could be observed. But these intercalated layeres remained organized, and some tactoids were still present. From (d) – (f) the effect of CO₂ pressure on clay structure during compounding could be observed. With the pressure increase, the average area of the tactoids increased, with $2.35 \times 10^5 \text{ nm}^2$, $3.48 \times 10^5 \text{ nm}^2$ and $6.11 \times 10^5 \text{ nm}^2$ respectively calculated by the software SigmaScan; a particle size distribution could not be determined due to the compact arrangement of individual clay structures within the swollen mass. It was found that pressure had a strong effect on the morphology of surfactant within the clay. With the increasing of gas pressure, the mobility of the surfactant/compatibilizer increased due to the plasticizing effect by CO₂

within the interlayer region. In regards to the surfactant, the presence of scCO_2 helped achieve a more complete oleophilic coating over all galleries. This increased uniformity in surfactant dispersion within the clay interlayers would allow greater penetration of polymer species (i.e. MA-PP chains) into the clay structure and a weakening of the van der Waals forces between adjacent silicate sheets, which led to a greater chance for delaminate in a shear flow. On the other hand, the presence of scCO_2 in the polymer phase was likely to increase the inter-chain distance and free volume, and reduce the inter-chain interactions. Thus, scCO_2 also leads to significant changes in properties of polymers such as lowering the viscosity of the polymer melt [Ma et al. 2007], which aids its intercalation into the galleries but would limit shear transmission during the delamination step. It was well known that a reduction in polymer melt viscosity is dependent on the concentration and pressure of CO_2 [Royer et al. 2001; Bortner and Baird. 2004]. With the gas pressure increasing, the viscosity dropped and thus there was insufficient shear stress to delaminate the clay particles merely expand their coverage area.

To highlight the effect of moderate shear mixing by the TSE without the presence of CO_2 on the already swollen SSE-developed structures from Figure 4.2.8, Figure 4.2.9 shows the clay structure of Sample 16 and 20 which were before and after twin screw extrusion, respectively. Both pictures were taken in larger magnification at 200,000. Figure 4.2.9 (a) shows a typical intercalated stack from the SSE without the dispersion of individual layers but the structure remained loose. Figure 4.2.9 (b) demonstrated the structural changes after shear mixing in twin screw extruder of the same sample. Despite the layer stacks still partially remaining, these stacks became thinner and a lot of exfoliated particles were found. The author suggests that a longer twin screw extruder, which could afford sufficient mixing after gas removal, would be favourable to optimize this processing approach.

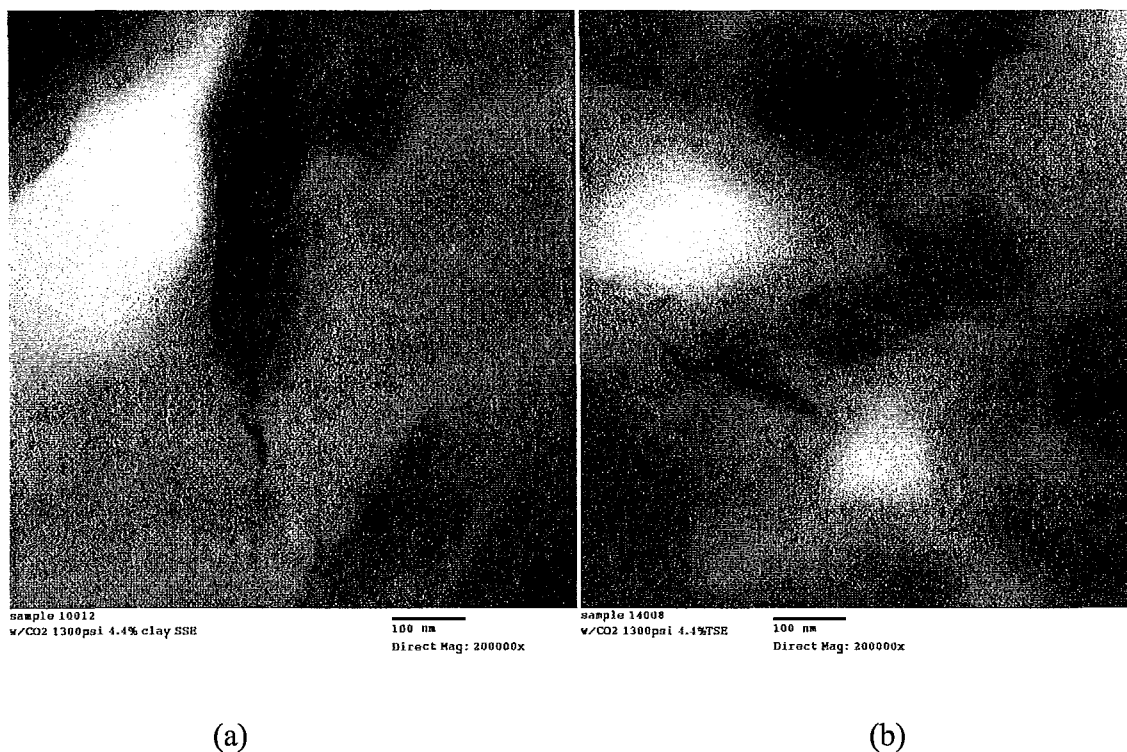
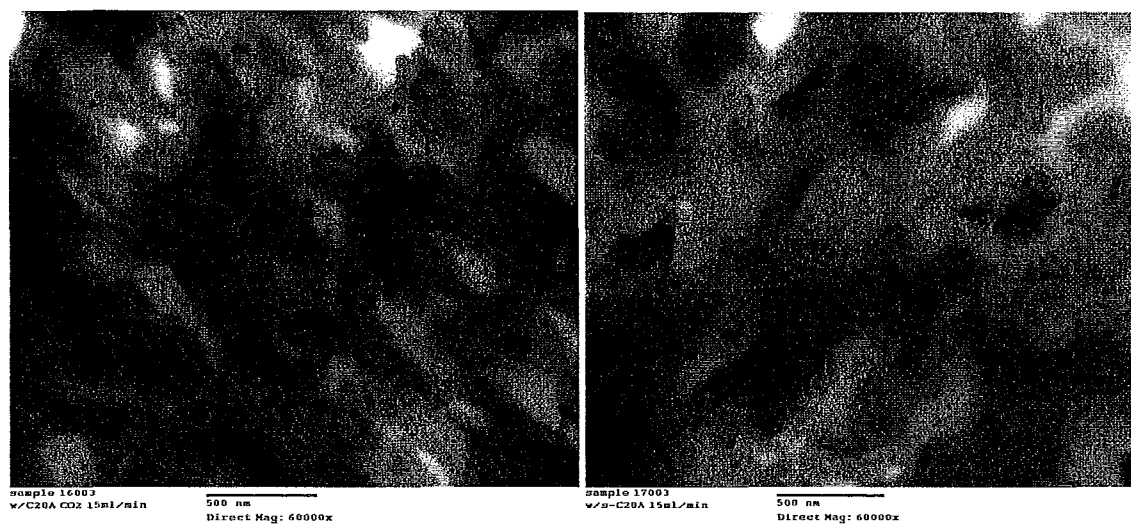


Figure 4.2.9 TEM micrographs at 200,000 magnification for Samples 16 (a) and Sample 20 (b) in Method 3

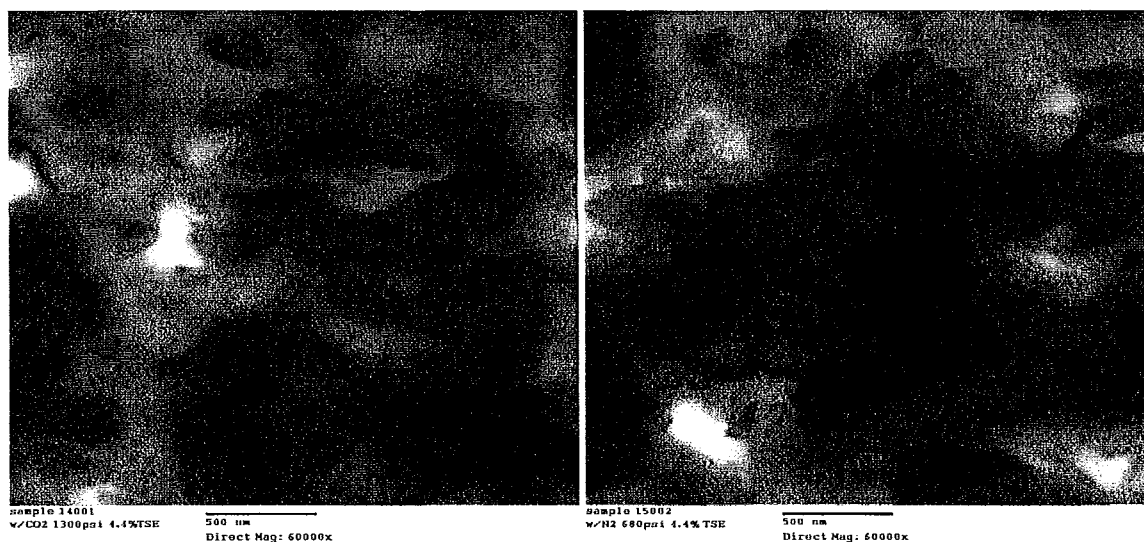
Figure 4.2.10 shows the TEM micrographs for samples in **Group Two**, which refers to the *incomplete exfoliation* structure with exfoliated particle and intercalated tactoids present. The dark lines in the micrographs indicate tactoids with thicknesses ranging from 5 to 20 nm, and the grey silhouettes indicate individual platelets dispersed in the polymer matrix. Particle size determination by image analysis was conducted for four nanocomposites prepared in CO₂ or in N₂. The normalized frequency distribution of the clay tactoids are summarized in Figure 4.2.11. Of these samples, the one compounded within a nitrogen environment (d) had the poorest exfoliation. Among the other three nanocomposites using CO₂, the largest tactoids present were found in the nanocomposites filled with the as-supplied C20A clay and prepared with direct CO₂ injection. The other two samples shared similar features of clay dispersion with nanocomposite prepared by

Method 3 showing slightly better exfoliation compared to that based on s-C20A in Method 1. This result is consistent with the XRD diffraction patterns.



(a)

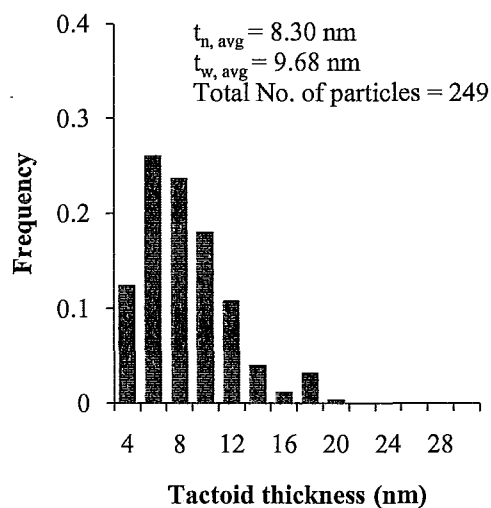
(b)



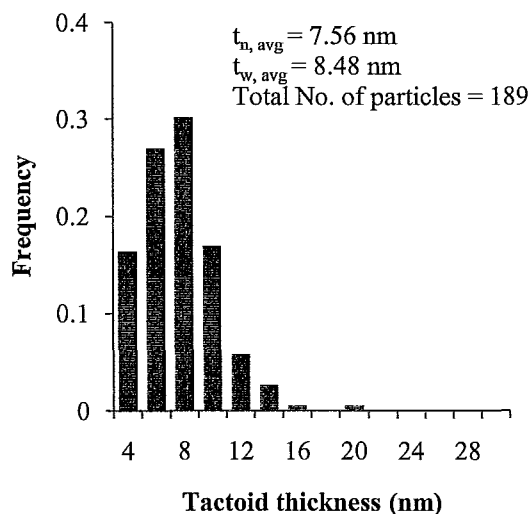
(c)

(d)

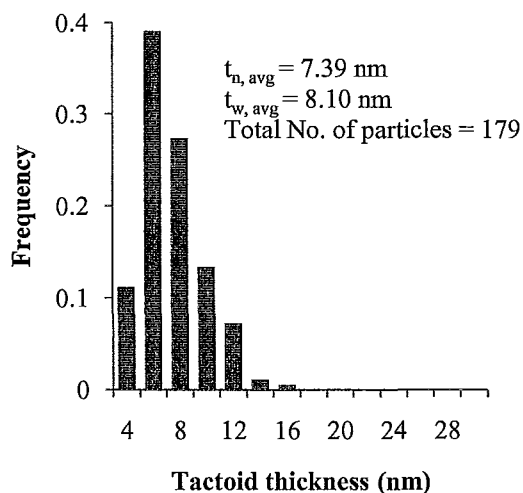
Figure 4.2.10 TEM micrographs for nanocomposites (a) Method 1, Sample 3 (b) Method 1, Sample 8 (c) Method 3, Sample 20 (d) Method 3, Sample 17



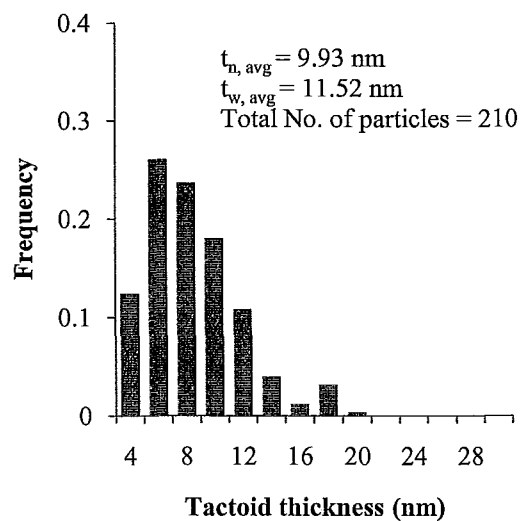
(a)



(b)



(c)



(d)

Figure 4.2.11 Histograms for tactoids thickness by image analysis of TEM micrographs of the TPO nanocomposites in Figure 4.2.10: (a) Method 1, Sample 3 (b) Method 1, Sample 8 (c) Method 3, Sample 20, (d) Method 3, Sample 17. Number average and weight average thickness are included.

4.2.4 Rheological properties

The rheological properties of a prepared nanocomposite tend to be more sensitive indicator for the state of exfoliation than many other techniques examined in the literature, particularly on a comparative basis. It also tends to correspond well with trends in mechanical properties and can be done using less material than a mechanical test. Measuring the storage modulus curve by an oscillating parallel plate rheometer (ARES) can reveal molecular information related to impeded segmental chain motion which helped to establish the microstructural features of the prepared composites.

Figure 4.2.12 compiles the storage modulus curves measured for nanocomposites prepared by Method 1 based on as-supplied C20A clay. The curves indicated no change in the microstructure of the prepared nanocomposites regardless of the concentration of CO₂ used during processing. No evidence was found that the scCO₂ aided clay exfoliation by this processing method.

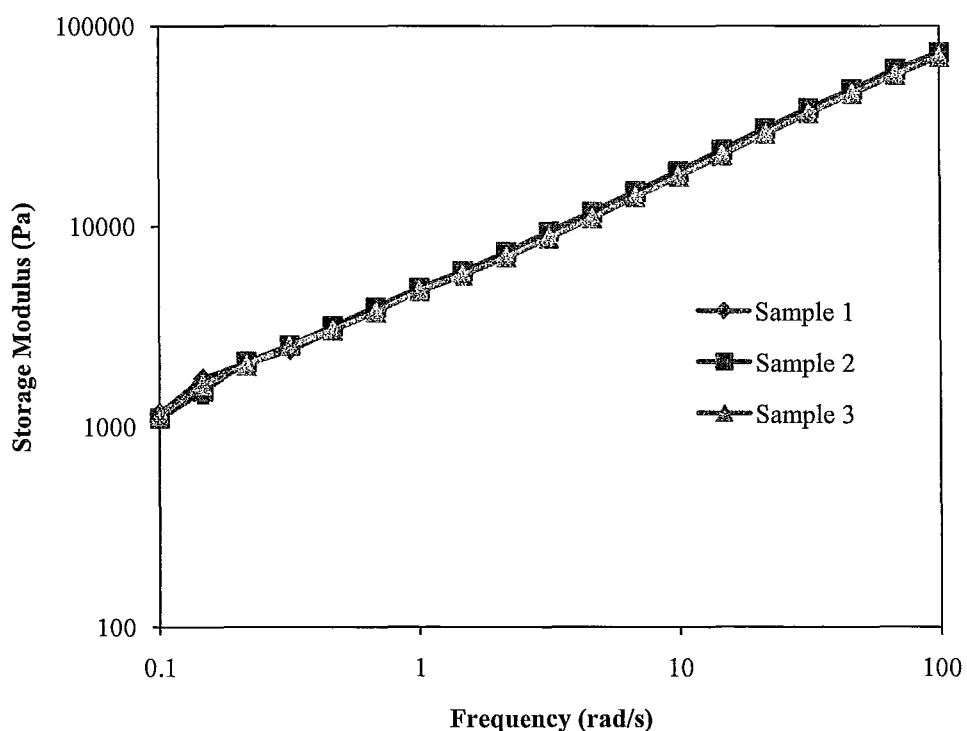


Figure 4.2.12 Storage modulus for TPO nanocomposites based on as-supplied C20A

The storage modulus for nanocomposites prepared with s-C20A compared with neat TPO was shown in Figure 4.2.13. These materials incorporating s-C20A demonstrated much more sensitivity to the influence of CO₂. Without the presence of scCO₂, the non-compatible s-C20A/TPO mixture (Sample 4) showed the lowest storage modulus of all samples prepared in these trials in spite of not including the diluting effect of the low viscosity MA-PP in its matrix. Conversely, s-C20A/TPO mixture with scCO₂ (Sample 5) showed the highest modulus of the set of materials created with this clay type. This suggests that the coating structure for the scCO₂ treated clay precluded interaction with the matrix but with the aid of scCO₂ during mixing diffusion of the matrix chains into the clay galleries was possible. The remaining samples (Sample 6-8) showed the diluting effect of the compatibilizer on the modulus of the nanocomposite and each gave similar curves.

It was observed that the storage modulus of nanocomposites increased compared to neat TPO and the slope become more negative at low frequency. It is well stated in literature [Litchfield et al. 2007] that the storage modulus of non-elastic polymers should tend toward zero at infinitely low frequency. For nanocomposites, a percolated network is formed, in which the nanofillers formed a gel-like structure within the polymer matrix due to strong interactions between nanofillers and matrix. When a network forms the storage modulus tend toward a plateau value at zero frequencies. It was also believed that the extent of percolated network can increase in two ways, one is by increasing the number of clay stacks and the other is increasing the level of exfoliation [Paul et al. 2007]. But in our case, those composites prepared with s-C20A demonstrated lower modulus compared to those with C20A, which was the opposite order to the level of exfoliation showed in XRD and TEM. The lower storage modulus might be attributed to the slight lower clay content (4.13 wt% vs. 4.71 wt%), but the effect should be minor. It appeared that pretreatment of C20A before mixing reduced the reinforcing capacity of the clay by its interaction with the matrix. This result was somewhat consistent with other researcher

[Liu et al, 2009], who found that improved exfoliation resulted in a lower storage modulus for the material produced under the influence of scCO_2 .

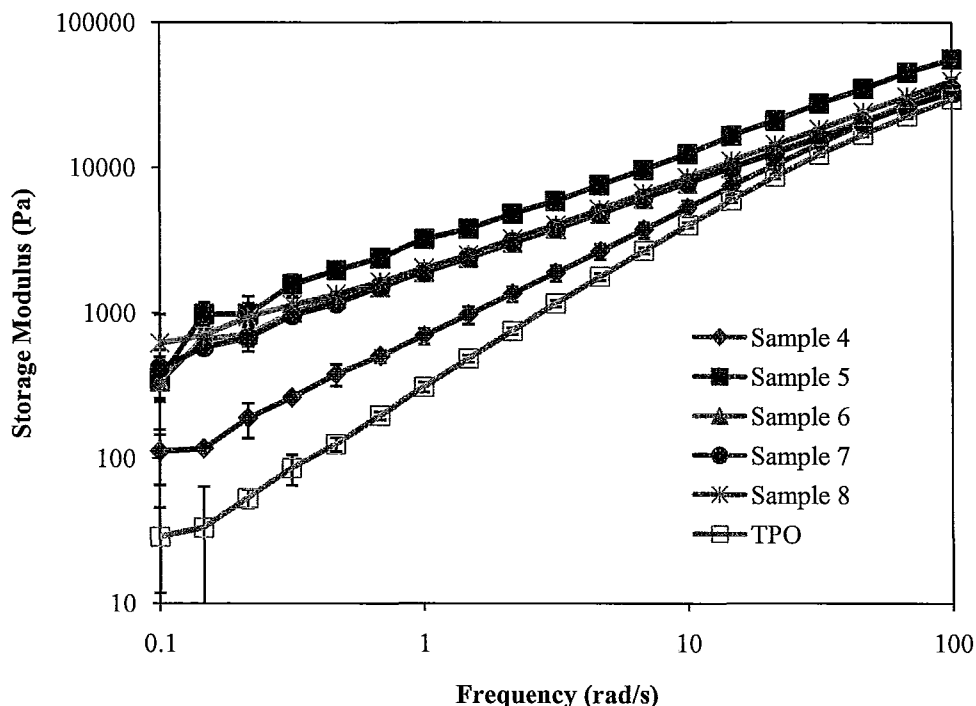


Figure 4.2.13 Storage modulus for TPO nanocomposites based on s-C20A

The dynamic viscosity for nanocomposites prepared by Method 1 and neat TPO is shown in Figure 4.2.14. The viscosity curves followed the same trend as that of storage modulus, with the nanocomposite based on as-supplied clay (Sample 3) exhibiting the highest viscosity. Just like the storage modulus discussed above, the TPO/s-C20A mixture without PB3200 exhibited the highest viscosity among the rest of the samples processed with the aid of scCO_2 . When the CO_2 was absent, poor interactions between non-polar TPO and clay led to the witnessed reduction in viscosity. For the three compatibilized nanocomposites which incorporated s-C20A (Sample 6-8), there was a slight increase in viscosity with increasing of CO_2 concentration. Unlike the neat TPO which had a Newtonian plateau at low shear rate, the intercalated nanocomposites displayed a shear-

thinning behaviour at the same shear range. This type of behaviour was typical of dispersed nanocomposites with good polymer/clay interactions.

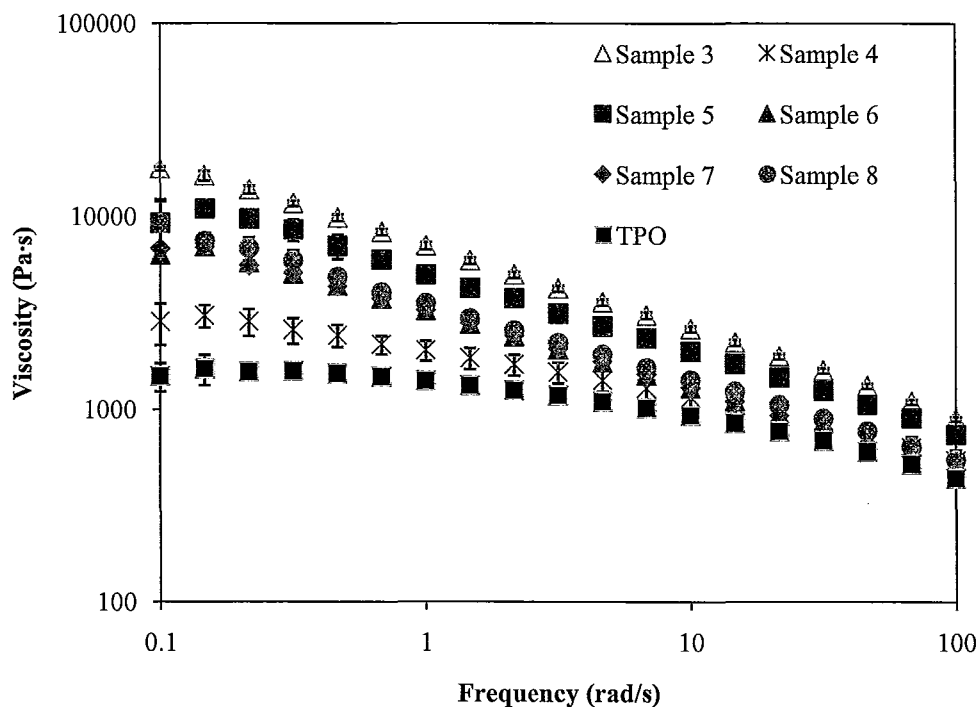


Figure 4.2.14 Dynamic viscosity for nanocomposites prepared in Method 1

Figure 4.2.15 shows the storage modulus curves for samples prepared by Method 2. All samples exhibit similar storage modulus and no evident effect of CO₂ was found. According to the XRD diffraction patterns and TEM micrographs, we know that although the clay layers were well intercalated within these samples these layers were still stacked together without uniform dispersion in the polymer matrix; surface area for stress transmission was not maximized. This might be a reason why the storage modulus did not increase for these samples. Moreover, it was surprising to see that the magnitude of the modulus for these nanocomposites were somewhat lower than neat TPO despite an approximate 5 wt% of clay loading for all these composites. This result led to suspicions

that the PB3200 was being degraded due to the high set-point temperature (300°C) of injector and therefore hurt the properties for final products.

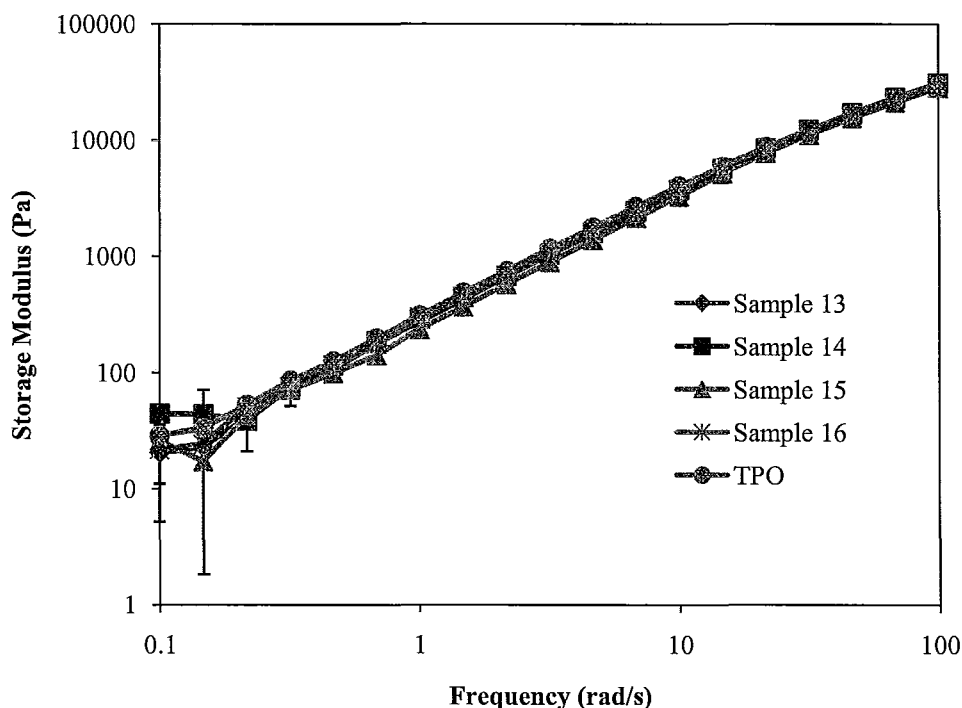


Figure 4.2.15 Storage modulus for samples prepared by Method 2

To examine the effect of degradation, a PB3200/C20A mixture treated to the same temperature (set point 300°C) and duration (80min), was collected from the injector, either under supercritical CO₂ (8.3 MPa) or nitrogen (4.1 MPa), respectively. Unfortunately, neat PB3200/C20A appeared so viscous that it torqued out the ARES rheometer, and its viscosity data was therefore, not available for comparison with the other two samples. This fact alone suggested that both materials collected from the injector had experienced degradation.

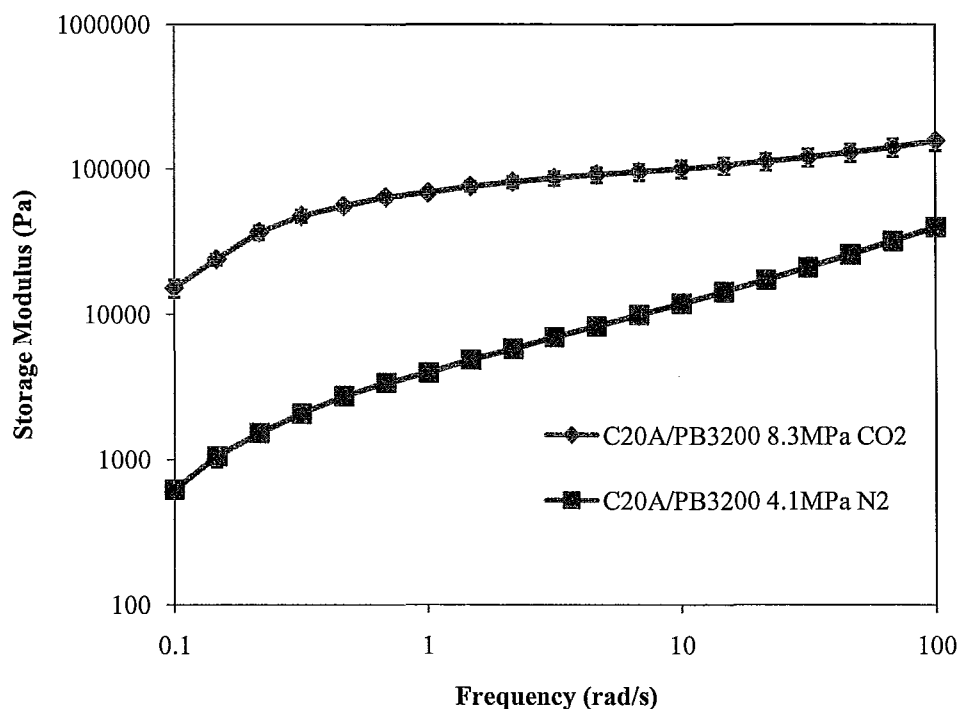


Figure 4.2.16 Storage modulus for C20A/PB3200 annealed in nitrogen and scCO₂

C20A treated by CO₂ was found to have an evident higher solid-like behaviour compared to that treated by nitrogen, which is shown in Figure 4.2.16. This result highlighted the effectiveness of scCO₂ solvent acting as a plasticizer, improving the interaction between compatibilizers and organoclay.

While the unprocessed PB3200/C20A mixture could not be analyzed, it was possible to examine the effect of degradation on the neat PB3200 alone, though its exhibits extremely low viscosity at high temperatures (180°C~200°C) prevented conventional analysis by the parallel plate rheometer. The viscosity of a nitrogen-treated PB3200 from the injector (300°C, 80 min) and as-received PB3200 were measured using an ATS Stresstech HR rheometer. A CO₂ sample was not collected since the intent of the test was merely to establish whether degradation was occurring. A 40 mm parallel plate was used and the

test temperature was set to 200°C. The result was shown in Figure 4.2.17. The rheological curves indicated an evident reduction in viscosity caused by injector. This result led to the development of a different heating approach, the new two-stage profile which was applied in Method 3, in order to minimize the degradation effect.

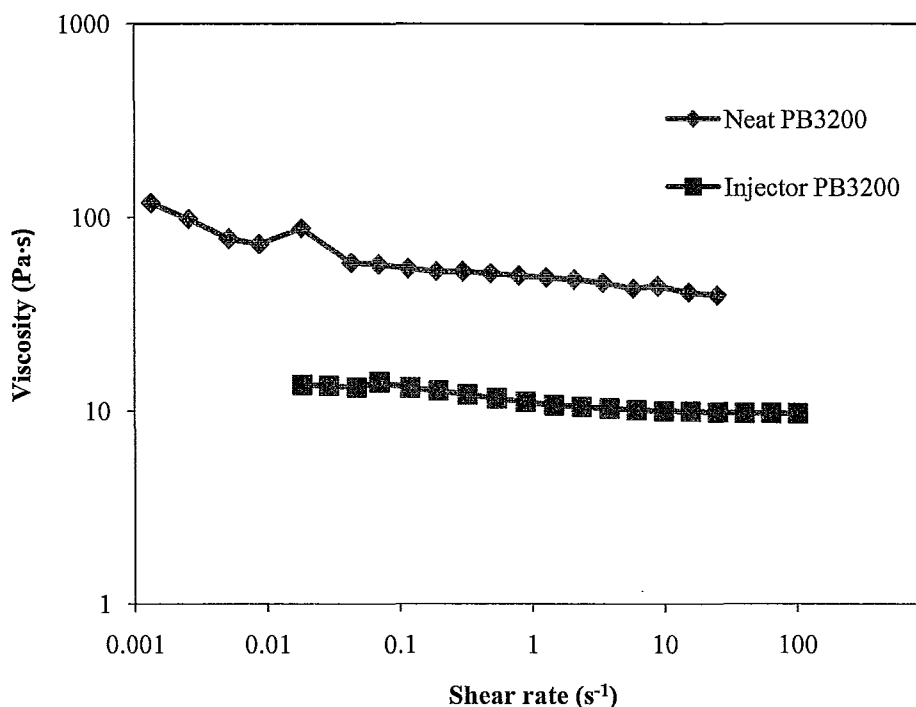


Figure 4.2.17 Viscosity for PB3200 before and after annealing in the injector

Figure 4.2.18 shows the storage modulus of all samples through the first-pass of SSE in Method 3 with neat TPO included as a benchmark. Although the TEM micrographs for all samples collected from first-pass single screw extrusion exhibited similar large stacks as those prepared by Method 2, all these samples demonstrated an evident increase in storage modulus compared to neat TPO, indicating that the two-stage heating is effective in minimizing the degradation of PB3200. Sample 13 showed a slight higher modulus, which was possibly attributed to the relatively higher clay content.

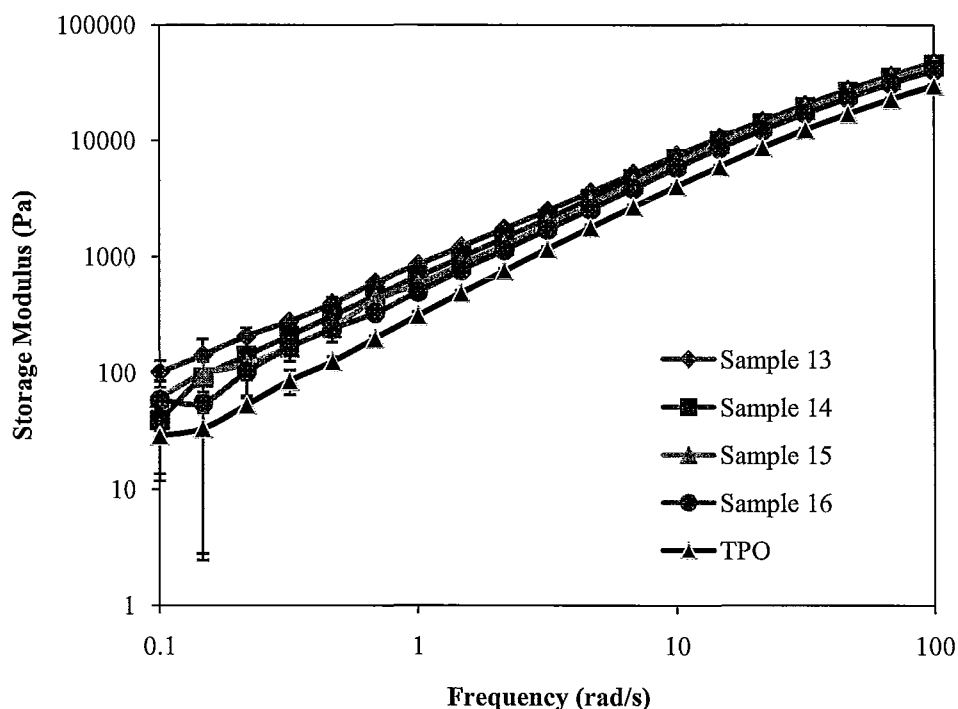


Figure 4.2.18 Storage modulus for nanocomposites through SSE in Method 3.

The storage modulus for those samples which passed through the twin screw extruder is shown in Figure 4.2.19. Sufficient shear force afforded by the twin screws without the presence of gas was found to be most effective in delaminating the stacks of silicate, which led to a further increase in the modulus. This result was consistent with the XRD and TEM results. But those nanocomposites compounded in higher pressure (Sample 19 and 20) did not show evident effects on the modulus. Since these high-pressure injected samples looked darker in colour, the author was suspicious of thermo degradation by PB3200 which might be attributed to the relatively longer residence time taken for melt compounding. For high-pressure injection trials, it took considerable longer time to build up back pressure in the extruder to push the clay out of the die. Simultaneously, it was also more time-consuming in building up higher pressure in the syringe pump. Samples 17, which was processed in nitrogen environment showed slightly higher modulus than

other samples prepared in CO₂. It appeared that the improved coating efficiency under CO₂ led to reduced interactions of the PB3200 with the clays.

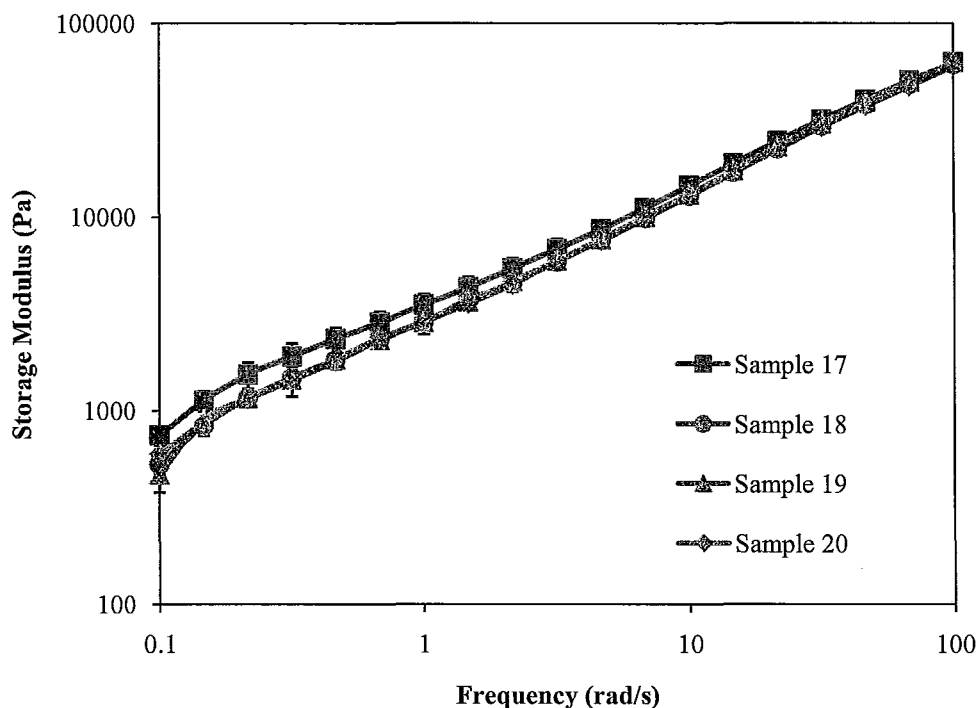


Figure 4.2.19 Storage modulus for nanocomposites through the TSE in Method 3

Figure 4.2.20 summarized a comparison between nanocomposites aided in their preparation by scCO₂ by one of two strategies: 1) *direct CO₂ injection* and 2) *clay/CO₂ suspension injection*. All samples exhibited considerable improvement compared to neat TPO. Injecting clay/CO₂ as a suspension improved the modulus compared to that of the s-C20A based nanocomposites, yet still their properties did not exceed the neat TPO nanocomposites without gas and using C20A. These results may be inferring what some molecular simulations [Totha et al. 2004] have concluded, that maleic anhydride grafted polypropylene interacts strongest when the silicate surface is exposed. In that case, the tendency of scCO₂ to improve surfactant coating uniformity in the clays may be interfering with stress transfer during shear mixing to cause clay delamination. We know

from our earlier results that the surfactant in the as-supplied organoclay materials was more likely to organize closer to the edges of the silicate sheets while as the gallery interior still contained sodium ions. It seems that an effective compatibilizing molecule must coordinate with the negatively charged silicate surface to bring about appropriate stress transfer from the matrix. Thus, exposing the clay together with the MA-PP compatibilizer to scCO₂ in the injector would be a better strategy. However, degradation problems should never be overlooked and are not easily overcome.

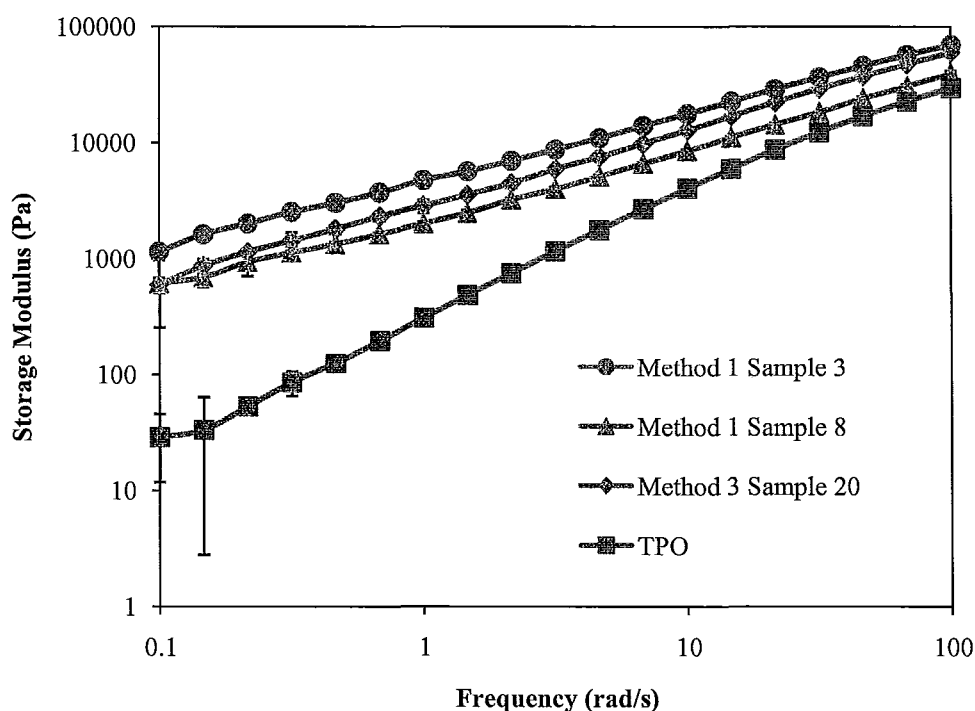


Figure 4.2.20 Summary of storage modulus for nanocomposites prepared by two main strategies: direct CO₂ injection vs. clay/CO₂ suspension injection

4.2.5 Mechanical properties

Flexural modulus is an important property for automotive materials, which refers to material's stiffness when flexed. The modulus for nanocomposites prepared by Method 1 and Method 2 are shown in Table 4.2.3 and Table 4.2.4.

Table 4.2.3 Flexural modulus of TPO nanocomposites prepared by Method 1

Sample #	1	2	3	4	5	6	7	8	TPO
Flexural Modulus (MPa)*	1021	1056	1049	904	959	932	938	938	744

* These values are supplied by General Motors, standard deviations not available

The flexural modulus corresponded well with the storage modulus results, though the magnitude of changes was smaller. For the TPO nanocomposites prepared with the as-supplied C20A (Sample 1-3), no evidence of change was found with the presence of CO₂. The flexural modulus for nanocomposites based on the pretreated clay (Sample 4-8) dropped in direct correspondence with the storage modulus at low frequency since both tests are deforming the materials at low strain rates. The CO₂ effect was observed evident for those uncompatibilized samples (Sample 4-5). Without the presence of scCO₂, TPO nanocomposite (Sample 4) had the lowest flexural modulus which could be attributed to the lower crystallinity in the final product and poor interactions with the clay. When scCO₂ presented (Sample 5), there was a moderate increase in crystallinity which led to a higher modulus but remained well below the as-supplied C20A sample. With the addition of PB3200 as a compatibilizer, the flexural modulus was again consistent with rheological properties.

The flexural modulus of TPO nanocomposites prepared by Method 2 was shown in Table 4.2.4, two benchmark samples were neat TPO with flexural modulus of 744 ± 35.3 MPa and Sample 8, which has a flexural modulus 923 ± 36.5 MPa, corresponding to the data provided by GM (938MPa). All samples prepared in Method 2 showed limited improvement in modulus, mostly due to poor disperse of the clay stacks in the polymer matrix. These data also followed the same trend as storage modulus.

Table 4.2.4 Flexural modulus of TPO nanocomposites prepared by Method 2

Sample #	9	10	11	12
Flexural Modulus (MPa)	772 ± 18.6	784 ± 19.4	799 ± 21.9	810 ± 14.0

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This thesis examined the current processing method for polyolefin PLS nanocomposites in comparison to approaches using scCO_2 as an exfoliating aid which included a novel *organoclay- CO_2 injection* method. The approaches from the literature included, i) the addition of a scCO_2 pretreated organoclay instead of an as-supplied organoclay, and ii) direct injection of scCO_2 into the extruder during mixing. In regards to the latter approach, the organoclay is combined with the polymer matrix and compatibilizer upstream of the gas injection. The new approach in this thesis was the addition of the organoclay in the presence of scCO_2 and maintaining that supercritical fluid state at least through the first stage of mixing as the clay is combined with the already molten polymer matrix and compatibilizer. To accomplish the goals of this new approach an organoclay- CO_2 injection apparatus was developed. Trials in both single screw and twin screw extruders were compared as a suitable methodology was developed. A series of samples were produced and characterized, and the conclusions are summarized as follows:

XRD patterns showed that the preconditioning of the C20A clay in scCO_2 increased the chain mobility of the alkylammonium surfactant within the clay interlayers, leading to rearrangement of surfactant and thus expanding the clay interlayer spacing. The XRD showed the distinct shoulder peak for as-supplied C20A based nanocomposites was significantly weakened for those s-C20A based ones, indicating s-C20A clays allowed greater intercalation of polymer chains and were more readily delaminated under shear mixing. The TEM graphs were consistent with XRD results, exhibiting better dispersions

for those s-C20A based specimens as well. However, this method appeared to reduce the reinforcing capacity of the clay through the interactions between scCO₂ and the polymer matrix. All s-C20A based nanocomposites showed reduction in rheological and mechanical properties even with an improved exfoliation. This result was found consistent with other researchers [Liu et al. 2009].

The *direct gas injection method* was found to have no effect on as-supplied C20A based nanocomposites, neither on morphology nor on end-use properties. While some materials based on s-C20A showed higher sensitivity to the scCO₂ injection during melt compounding. For uncompatibilized TPO/s-C20A mixtures, it was evident from the XRD patterns that polymer chains were more easily intercalated into these clay galleries with the aid of scCO₂ during mixing, which led to a subsequent improvement in storage modulus and flexural modulus. For compatibilized TPO/s-C20A mixtures, the influence of scCO₂ was minor, showing only a slight increase in storage modulus with the increase of CO₂ concentration.

The *clay-CO₂ injector* was designed to inject C20A/MA-g-PP mixtures at their molten state because the high cohesiveness of sole C20A and its mixture with MA-g-PP prevented flowing without extreme fluidization. Both XRD and TEM results demonstrated CO₂ was more favourable aiding intercalation over nitrogen. With increasing CO₂ pressure, the uniformity of the surfactant dispersion within clay galleries increased due to plasticization by the gas, which subsequently allowed greater intercalation of polymer chains and further delamination under shear mixing. However, both single screw extruder and twin screw extruder approaches could not provide sufficient shear force to bring about exfoliation while compounding in the presence of scCO₂ (due to its strong plasticizing effect that lower the viscosity of polymer melt). A second-pass through the twin screw extruder without gas was necessary to bring about more complete exfoliation. Despite the improvement in exfoliation led by this *clay-CO₂*

suspension injection method, the rheological properties remained below those untreated nanocomposites, possibly due to the thermo oxidative degradation on the compatibilizer. However, this method appeared to bring about improved storage modulus compared to the pretreated clay approach.

In summary, scCO₂ was found to be an effective exfoliation aid in both *pretreating clay approach* and *clay-CO₂ injection method*, according to XRD and TEM result. Maintaining either sole clay or with compatibilizer together in scCO₂ solution effectively expanded the clay interlayer spacing and made them ready for interaction with polymer chains during the compounding process.

5.2 Recommendations

The current screw design was found to be unsuitable for generating pressure higher than supercritical point of CO₂ in the injection zone. A new screw design should be developed for the next stage of the project. Considering the poor mixing with the presence of scCO₂ in polymer melt, a longer twin screw extruder which could provide sufficient shearing mixing after gas removal, would be favourable to further delaminating the clays. Otherwise, a second processing pass for higher intensity shear mixing is needed. Since the injector caused significant heating issues that led to the degradation of compatibilizer, a new apparatus which provides more effective heat transfer without extremes in temperature should be developed. A current being tested extensional strain mini-mixer with easy-going heat transfer is hopefully to minimize the degradation problems.

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