SYNTHESIS AND PROPERTIES OF
RUBBER-CLAY NANOCOMPOSITES

by

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Paulo Cesar Meneghetti
DEDICATION

I would like to dedicate this work to my entire family, most importantly to the love of my life, Inger, who has always been next to me on this long journey; to my parents who were always so proud and supportive of their youngest son; to the Birkholms’s for their enthusiastic influence; and to the little Camille who brought me a smile everyday.

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Synthesis and Properties of Rubber-Clay Nanocomposites

Abstract

by

PAULO CESAR MENEGHETTI

Styrene-butadiene (SBR)/clay nanocomposites were synthesized via mechanical mixing using a Brabender mixer and 2-roll mill. The montmorillonite (MMT) used was functionalized with four different surfactants: commercially available octadecyl-amine (C18amine) and laboratory synthesized octadecyldimethyl-betaine (C18DMB), vinylbenzyl-dodecyldimethylammonium chloride (VDAC), and vinylbenzyl-octadecyldimethylammonium chloride (VODAC). The surfactant chain length and functional groups affected the dispersion of clay nanolayers in the matrix and the properties of the nanocomposites. Partially-exfoliated SBR nanocomposite obtained with VODAC-MMT presented the greatest mechanical reinforcement and oxygen barrier: elastic modulus at 25°C was 14 times higher than SBR, and oxygen permeability was reduced by 60% with 15 wt.% silicate. Nielsen model was used to fit the permeability data and to calculate the filler aspect ratio, which was also determined by Transmission Electron Microscopy. The best performance of nanocomposites containing VODAC-MMT is attributed to the presence of the vinyl-benzyl group in the surfactant, which provides higher compatibility with SBR and greater dispersion of the organoclay, increasing the tortuous path for gas diffusion through the rubber.
Furthermore, the addition of carbon black to SBR and to SBR/clay nanocomposites was investigated. While carbon black alone (40 phr) offered great improvement in the mechanical properties of the rubber, the synergism of organoclay and carbon black brought similar property enhancements with only half the total filler loading (10 phr each filler). The oxygen permeability of the two-filler system was also lower than for SBR containing only carbon black.

Two other types of rubber/clay nanocomposites were synthesized: natural rubber (NR) and bromo-butyl rubber (Br-IIR). Oxygen barrier for both nanocomposites was higher than pure rubber or conventional composite. The types of surfactant used to modify MMT led to different clay morphology in the matrix, affecting the tortuosity for gas diffusion.

Significant enhancements in mechanical, thermal, and barrier properties were demonstrated for rubber/clay nanocomposites. In addition, a nanocomposite gel electrolyte consisting of poly(methyl methacrylate) (PMMA)/clay, ethylene carbonate/propylene carbonate as plasticizer, and lithium perchlorate was synthesized for electrochemical studies. Ionic conductivity varied slightly, exhibiting a maximum of \(8 \times 10^{-4} \text{ S/cm} \) with 1.5 wt.% clay at 25°C, and stable lithium interfacial resistance was observed over a three-week storage period.
CHAPTER 1
GENERAL INTRODUCTION

1.1. BACKGROUND

Polymer composites are widely used in a variety of applications involving construction, transportation, electronics, and consumer products. The properties of particle-reinforced polymer composites are strongly influenced by the dimensions and microstructure of the dispersed phase. In recent years, polymer-clay nanocomposites have drawn great interest from both the industry and academia because they often exhibit remarkable improvements in materials properties at very low clay loading (up to 10 wt.%) when compared to pristine polymer or conventional composites [1-4]. Nanocomposites constitute a new class of material having nano-scale dispersion, typically 1-100 nm, of the filler phase in a given matrix [5, 6]. The outstanding reinforcement of nanocomposites is primarily attributed to the large interfacial area per unit volume or weight of the dispersed phase (e.g. 750 m²/g). The nanolayers have much higher aspect ratio than typical microscopic aggregates [7-9]. Mineral clays which can be dispersed as silicate nanolayers of high aspect ratio are attractive for polymer reinforcements. Polymer-clay nanocomposites have shown drastically enhancements in mechanical properties (modulus and strength) [10-13], thermal properties (heat resistance and flammability) [6, 14], barrier properties [15-21], and biodegradability [22, 23] of the pure polymer.

The colloidal state and the surface chemistry of the silicate layers in the polymer matrix play important roles in the synthesis of polymer-clay nanocomposites.
Electrostatic forces maintain the clay layers together forming face-to-face stacks in agglomerate tactoids which complicate their dispersion in polymers [24]. Also, the incompatibility between the hydrophilic clay and the hydrophobic polymer hinders nanoscale dispersion of the clay. In order to achieve a high degree of dispersion, the silicate layers can be functionalized by adsorption of organic molecules such as surfactants to diminish the surface forces contributing to layer-stacking. Intercalation of organic molecules modifies the hydrophilic surface into hydrophobic, raising the level of compatibility between the clay and the polymer. Intercalation can be achieved in the clay interlayers by ion exchange of cations loosely held by the negatively charged layers. Polar organic molecules replace these cations rendering the clay organophilic.

The fast pace of research in polymer-clay nanocomposites has already developed some products that are being used commercially for certain applications such as automotive with nylon nanocomposites (the most utilized system) in timing belt cover for automobiles [25], and in packaging film [26]. Other nanocomposite systems that have been extensively reported in the literature include polymer matrices such as polystyrene, poly(methyl methacrylate), polyolefins, poly(ethylene oxide), polyimide, poly(vinyl pyrrolidone) and epoxy. This chapter provides a review of the clay structure and recent developments in the synthesis and properties of modified clay and polymer-clay nanocomposites.

1.2. CLAY STRUCTURE AND CATION EXCHANGE WITH SURFACTANTS

Clay minerals consist of a group of hydrous layered magnesium- or alumino-silicates (phylllosilicates). Each phylllosilicate is essentially composed of two types of sheets, octahedral and tetrahedral, designated O and T, respectively [8-9, 24, 27]. In the
tetrahedron, Si$^{4+}$ is surrounded by four O$^{2-}$ in the corners; three of the four oxygens are simultaneously attached to adjacent tetrahedrons. These connecting oxygen atoms are arranged in-plane so as to create a net of surfaces with six tetrahedrons arranged in rings. The tetrahedral layers are interlinked at their vertices by metal ions such as Al$^{3+}$ and Mg$^{2+}$. The connecting cations are arranged in octahedral coordination, with free valences saturated by O$^{2-}$ and/or OH$^-$ ions. The tetrahedral and octahedral sheets can be stacked on top of each other to form two basic types of clay structure: TO or TOT. Kaolinite is the most common mineral of the non-expanding TO type group. In the kaolinite clay layer, oxygens located at the apices of the silicate tetrahedra of the tetrahedral sheet and hydroxyls of one of the two OH planes of the octahedral sheet are condensed, forming a single plane common to both sheets. In the other basic clay structure, TOT, four main groups can be distinguished: talc-pyrophyllite, smectite (montmorillonite), vermiculite, and illite. Only smectite and vermiculites are expanding type clays.

The most commonly used layered silicates for the preparation of polymer-clay nanocomposites belong to the TOT family, in particular montmorillonite (MMT), shown in Figure 1.1. The layer thickness is around 1 nm, and the lateral dimensions of these layers can vary from 100 nm to several microns. Stacking of the layers leads to a regular van der Waals gap between the layers called interlayer or gallery. The isomorphous substitution within the layers (i.e. Al$^{3+}$ in the aluminate sheet with Mg$^{2+}$) generates negatively charged layers, which are then balanced by alkali and alkaline earth cations (Na$^+$, K$^+$, Ca$^{2+}$) to maintain charge neutrality [8]. These cations are arranged in between the parallel-superimposed layers. One particular characteristic of these silicate layers is a moderate surface charge known as cation exchange capacity (CEC), generally expressed
as mEq/100 g. This charge is not locally constant; it varies from layer to layer, and must be considered as an average value over the whole crystal [4].

Montmorillonite is originally hydrophilic, and must be converted to hydrophobic or organophilic nature in order to make it compatible with polymer matrices. Normally, this can be done via ion exchange of the inorganic cations for organic ones such as from surfactants and polyelectrolytes. Ion exchange reactions depend on the CEC of the clay. The organic cations lower the surface energy, and improve the wetting and intercalation of the polymer matrix, resulting in a larger interlayer spacing. Additionally, the organic cations may provide functional groups that can react with monomer or polymer to enhance interfacial adhesion between the clay nanolayers and polymer matrix [3, 28].
Extensive research has been devoted to the understanding of ion exchange and adsorption of surfactant molecules into the clay surface and gallery since organoclays are used in many industrial applications (i.e. thickeners in paints, oil-based glue, grease, and cosmetic products) [8, 29]. The negatively charged clay layers attract the organic cations primarily by electrostatic forces. In addition, van der Waals forces act between the flat oxygen planes and the organic species located in the interlayers. With increasing the size of the adsorbed organic cation, there is an increase in the sorption energy as the van der Waals contribution to the adsorption process becomes more significant [8]. Due to the increase in the van der Waals interactions, montmorillonites have high affinity towards long chain organic cations. Many surfactants including primary, secondary, tertiary and quaternary alkylammonium cations are water soluble, and most cation exchange reactions are performed in aqueous suspensions. Another point about the surfactant adsorption onto the clay layers is that it is not controlled by the critical micelle concentration (CMC) of the surfactant solution [30].

Several characterization techniques such as adsorption isotherm and precise calorimetry can be used to determine the type of adsorption and quantify the interactions between cationic surfactants and clay [31]. In addition, x-ray diffraction determines the increase of the gallery spacing in the clay due to surfactant intercalation, which has prompted speculations about the orientation and arrangement of surfactant in the interlayer. The type of clay and alkyl chain length of the surfactant affect the amount and the enthalpy of adsorption (exothermic) as well as the surfactant arrangement inside the gallery: either parallel or tilted, as monolayer, bilayer, or triple layer. These arrangements will be discussed in more detail in Chapter 2.
1.3. NANOCOMPOSITE STRUCTURE

This new class of material involves nano-scale dispersion in a polymer matrix, which leads to improved properties over regular composites. The complete dispersion or exfoliation of the clay layers in the monomer or polymer may comprise up to three steps similar to dispersion of powders in liquid, described by Parfitt [32]. The first step is wetting the surface of clay tactoids by monomer or polymer molecules. Secondly, intercalation or infiltration of the monomer or polymer takes place, followed by the third step, exfoliation of the clay layers. Thermodynamics controls the first and second steps, while mechanical and reaction driving forces determine the extent of the third step. Depending on the strength of interfacial interactions between the polymer matrix and the silicate layers, three types of polymer composites may be formed as shown in Figure 1.2. In conventional composites, the clay tactoids exist in their original aggregated state with nanolayers stacked face to face and without any polymer intercalation, which results in poor mechanical properties. In the case of intercalated polymer-clay nanocomposite few molecular layers of polymer penetrate the clay host galleries increasing the d-spacing. And finally, exfoliated polymer-clay nanocomposites contain individual nanolayers separated in a continuous polymer matrix by an average distance which depends on the clay loading. Usually, the clay content of an exfoliated nanocomposite is lower than that of an intercalated nanocomposite. Exfoliation is more appealing for enhancement of certain properties of the material because of the high degree of dispersion and maximum interfacial area between polymer and clay [33].
1.4. SYNTHESIS AND PROPERTIES OF POLYMER-CLAY NANOCOMPOSITES

1.4.1. Synthesis methods

Polymer-clay nanocomposites can be synthesized via four approaches depending on the starting materials and the processing techniques [3]. The first approach is via \textit{in situ} polymerization which consists of swelling the organophilic clay layers in the presence of liquid monomer followed by polymerization. It can be initiated by either heat or radiation, by diffusion of an appropriate initiator, or by a catalyst attached inside the clay via ion exchange. The ability of the small monomer molecules to intercalate in the nanolayers for polymer formation to occur makes this technique very successful in
achieving fully exfoliated layers. The disadvantage is the limitation of polymers/monomers that can intercalate directly into the clay gallery.

Emulsion polymerization is another method where the layered silicate is dispersed in an aqueous phase in the presence of a surfactant. The surfactant is not necessarily cationic; it can be anionic or zwitterionic. The monomer is added to the solution and adsorbs onto the clay layers. The advantage is the fact that the clay is modified in the same solution where polymerization occurs rather than functionalizing the clay in a separate stage as done for in-situ polymerization. Along the solution scheme, a third type of synthesis involves dissolving a polymer in a solvent, mixing with organoclay-solvent dispersion where the polymer will displace the solvent and intercalate within the interlayer. The solvent is finally removed, yielding the nanocomposite.

The fourth technique, melt intercalation, is more industrially favorable due to its ease of implementation and production, but results in a loss of control over the molecular weight of the final polymer [34]. This method consists of annealing, statically or under shear, a mixture of polymer and treated clay at a temperature above the glass transition or melting temperature of the polymer. A majority of nanocomposites can be synthesized with this approach.

1.4.2 Examples of Polymer Clay Nanocomposites

Nanocomposite technology has reached a variety of polymers systems that can be mixed with layered silicates. This section will focus on the different synthesis and properties of certain nanocomposites such as Nylon 6, polystyrene (PS), epoxy, polypropylene (PP), polyimide, and poly(methyl methacrylate) (PMMA).
1.4.2.1 Nylon 6-Clay Nanocomposites

The Toyota research group was the pioneer in polymer nanocomposites by synthesizing Nylon 6-clay nanocomposite via in-situ polymerization of $\varepsilon$-caprolactam in the clay interlayers [1, 10, 35]. Montmorillonite was modified with $\sigma$-amino acids [$\text{H}_3\text{N}^+\text{(CH}_2\text{)}_{n-1}\text{COOH}$] and it was demonstrated that the surfactant chain length affected the final morphology of the nanocomposite. The protonated alkylammonium cations catalyzed the intragallery ring-opening polymerization of caprolactam, providing a driving force for exfoliation of the nanolayers. For the system using 12-aminolauric acid, transmission electron microscopy (TEM) and x-ray diffraction (XRD) revealed complete delamination of individual clay layers homogeneously dispersed in the matrix. Mechanical properties showed significant improvements with the addition of only 4.2 wt. % of modified MMT (Table 1.1). These exfoliated nanocomposites demonstrated also significant increase in dimensional stability and barrier property [36].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Units</th>
<th>Nylon clay hybrid</th>
<th>Nylon 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>MPa</td>
<td>97.2</td>
<td>68.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32.3</td>
<td>26.6</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>Gpa</td>
<td>1.87</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.61</td>
<td>0.19</td>
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<tr>
<td>Flexural Strength</td>
<td>MPa</td>
<td>143</td>
<td>89.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32.7</td>
<td>12.5</td>
</tr>
<tr>
<td>Flexural Modulus</td>
<td>GPa</td>
<td>4.34</td>
<td>1.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.16</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Table 1.1. Mechanical properties of nylon 6-clay hybrid [10].

The enhancement in properties of nanocomposites led to further researcher from other groups in the polymerization of caprolactam or different techniques to make Nylon 6-clay. Messermith and Giannelis [17] polymerized $\varepsilon$-caprolactam inside clay gallery
modified by protonated aminolauric acid at high temperature. The exfoliated nanocomposite containing 4.8% silicate by volume showed a reduction in water vapor permeability of almost an order of magnitude over pure poly(ε-caprolactam) [17]. Cho and Paul [37-38] prepared Nylon 6-clay nanocomposites via direct melt compounding using a twin screw extruder. The mechanical properties and morphology of these nanocomposites were similar to the ones prepared by in situ polymerization. In fact, the twin screw generated higher shear than single screw extruder and led to complete exfoliation of the clay layers.

1.4.2.2 Polystyrene-Clay Nanocomposites

Polystyrene (PS) is one of the most researched nanocomposite systems, being synthesized via in-situ and emulsion polymerization, and by melt intercalation. There are several literature papers on polystyrene nanocomposites from different research groups. Akela and Moet [39] synthesized intercalated nanocomposites by using MMT modified via cation exchange with a polymerizable surfactant, (vinylbenzyl)trimethyl ammonium chloride. Styrene was in-situ polymerized in the presence of a solvent to facilitate intercalation. Do and Cho [40] also synthesized intercalated PS nanocomposite but without the use of solvent. By functionalizing MMT with different surfactants that contained tetraalkylammonium cations, the modified clay was directly dispersed in styrene followed by polymerization. These intercalated polystyrene nanocomposites exhibited enhanced thermal properties than pure polystyrene. Similar results were also reported by Weimer et al. [41].

Exfoliated PS-clay nanocomposite was synthesized by Fu and Qutubuddin (Figure 1.3a) via in situ polymerization of styrene with a reactive organoclay [11, 33].
MMT was functionalized with a polymerizable cationic surfactant vinylbenzyl-dimethyldodecylamonium chloride (VDAC). The storage modulus of the nanocomposite was higher depending on the clay loading when compared to pure PS, as illustrated in Figure 1.3b. Also, both intercalated and exfoliated structures were observed for PS-clay nanocomposite synthesized via melt intercalation [5, 42-44], while emulsion polymerization produced only intercalated hybrid [45].

Figure 1.3a. TEM of exfoliated PS/clay nanocomposite 5.6 wt% VDAC-MMT.
The use of clay filler with epoxy resin has also been studied by several research groups. The studies revealed clay intercalation as well as exfoliation, and were focused on the use of diglycidyl ether of bisphenol A [EPON-828] as epoxy resin. The composites were synthesized via \textit{in-situ} technique. Qutubuddin and coworkers [46, 47] synthesized epoxy resin cured in the presence of organophilic montmorillonite (OMMT) and intercalation was observed due to high interlayer spacing verified by both XRD and TEM. Several OMMTs were used, each derived from a different surfactant. The surfactants were tyramine hydrochloride, aminolauric acid, and a polyamide curing agent. XRD data indicated that generally the intercalated d-spacing was around 1.3-1.4 nm, and an extreme case had a 4.2 nm increase in the basal spacing. MMT modified with

Figure 1.3b. DMA scans of pure polystyrene and PS-clay nanocomposites [11].

1.4.2.3 Epoxy Resin-Clay Nanocomposites

The use of clay filler with epoxy resin has also been studied by several research groups. The studies revealed clay intercalation as well as exfoliation, and were focused on the use of diglycidyl ether of bisphenol A [EPON-828] as epoxy resin. The composites were synthesized via \textit{in-situ} technique. Qutubuddin and coworkers [46, 47] synthesized epoxy resin cured in the presence of organophilic montmorillonite (OMMT) and intercalation was observed due to high interlayer spacing verified by both XRD and TEM. Several OMMTs were used, each derived from a different surfactant. The surfactants were tyramine hydrochloride, aminolauric acid, and a polyamide curing agent. XRD data indicated that generally the intercalated d-spacing was around 1.3-1.4 nm, and an extreme case had a 4.2 nm increase in the basal spacing. MMT modified with
tyramine provided the best performance with the epoxy. Also, the addition of epoxiphylic polyamide-MMT reduced residual stress the most, approximately 50-60%. Dynamic scanning calorimeter (DSC) measurements showed that the $T_g$'s were higher than for the pure resin. It was clearly illustrated that the functional group used to modify clay significantly influences the behavior of the nanocomposite.

Exfoliated nanocomposites were also synthesized using modified clay layers in the epoxy matrix. Professor Pinnavaia’s research group at Michigan State University synthesized composites using EPON-828 with $\text{H}^+$, $\text{NH}_4^+$, $[\text{H}_3\text{N}(-\text{CH}_2)_n\text{CH}_3]^+$, $[\text{H}_3\text{N}(-\text{CH}_2)_{n-1}\text{COOH}]^+$, $[\text{H}_3\text{N}(-\text{CH}_2)_n\text{NH}_2]^+$, and $[\text{H}_3\text{N}(-\text{CH}_2)_n\text{NH}_3]^2+$ - exchanged forms of MMT, where $n = 6$ and 12 [2, 48, 49]. XRD and TEM confirmed the delamination of the clay layers in the polymerized epoxy resin. A 5 wt.% of $[\text{H}_3\text{N}(-\text{CH}_2)_n\text{COOH}]^+$ - MMT – polyether nanocomposite revealed that the interlayer spacing ranged up to 200 nm. Longer linear alkyl chain lengths benefited gallery accessibility and facilitated the formation of nanocomposite. The mechanism of exfoliation was dependant on the accessibility of the epoxy and its curing agent to the clay galleries and on the relative rates of intra- and extragallery network formation. In the $[\text{CH}_3(-\text{CH}_2)_{17}\text{NH}_3]^+$ - MMT / EPON-828 system, more than a 10-fold increase in tensile strength (8 MPa) and tensile modulus (25 MPa) was obtained by addition of only 15 wt.% of organophilic MMT. This was due to the fact that the rubbery epoxy allows the silicate particles to align to best resist the applied stress.

Messersmith and Giannelis [6] maximized the interfacial adhesion between the epoxy and the silicate layers leading to exfoliated nanocomposites with enhanced mechanical properties. The dynamic storage modulus ($E'$) in the glassy region below $T_g$
was 58% higher for the nanocomposites versus the pure epoxy with 4% by volume of clay loading. The rubbery plateau was also 4.5 times higher than unmodified epoxy.

1.4.2.4 Polypropylene-Clay Nanocomposites

One of the most used polyolefins in the industry is polypropylene. One obstacle for synthesizing nanocomposites in this system is the thermodynamic incompatibility between PP and organoclay since PP does not contain any polar groups in its backbone [50-52]. However, Toyota research group developed PP-clay hybrid by using simple melt mixing of three components: PP, maleic anhydride modified propylene oligomers (PP-MA), and clay intercalated with stearylammonium cation. XRD and TEM indicated that both intercalated and exfoliated composites were produced, depending on the type of maleic anhydride groups used: intercalated for PP-MA 1010 (acid value = 52 mmol of KOH/g) and exfoliated for PP-MA 1001 (acid value = 26 mmol of KOH/g). It was concluded that two factors influence the exfoliation and homogeneous dispersion of the layers in the hybrid: (i) the intercalation capability of the oligomers in the layers, and (ii) the miscibility of the oligomers with PP. In terms of improved properties, PP-clay hybrids exhibited higher storage moduli compared to that of PP especially in the temperature range from $T_g$, which is 13°C, to 90°C.

1.4.2.5 Polyimide-Clay Nanocomposites

Polyimide-clay nanocomposites have demonstrated a great improvement in barrier properties with a very small clay content. The nanocomposites were synthesized from polymer solution: 4,4’-diaminodiphenyl ether and pyromellitic dianhydride were polymerized in dimethylacetamide (DMAC) solvent, followed by mixing of the
poly(amic acid) solution with organoclay dispersed in DMAC [15, 19]. Clays with
different aspect ratios were used (hectorite 46, saponite 165, montmorillonite 218 and
synthetic mica 1230 [19]. XRD and TEM indicated primarily exfoliated nanocomposites
with mica and MMT, while monolayer intercalation was observed with hectorite and
saponite. The permeability of several small gases such as O₂, H₂O, and He, decreased
tremendously with clay content. For instance, with 2.0 wt.% of mica, the water vapor
permeability decreased to less than one tenth of that of unfilled polyimide. Lan et al. [16]
used a similar procedure to prepare polyimide nanocomposite MMT modified with
octadecylamine but obtained only intercalated hybrid. Still, the CO₂ permeability
decreased significantly by 80% with 7% volume fraction of clay. Such a decrease was
justified by a staircase alignment of the flakes, which can provide high tortuosity for the
diffusing gas.

1.4.2.6 Poly(methyl methacrylate)-Clay Nanocomposites

The synthesis of PMMA-clay nanocomposite has been reported recently using a
variety of surfactants, dispersion techniques and polymerization conditions [53-60]. Lee
and Jang [53] were the first to report synthesis of PMMA nanocomposite via emulsion
polymerization, which was carried out at 70°C for 12 hours. Their results, using an
anionic surfactant, sodium dodecyl sulfate (SDS), indicated an intercalated hybrid.
Bandyopadhyay et al. [56, 57] synthesized PMMA nanocomposite via emulsion
polymerization at 80°C with SDS as the emulsifier and 5 wt.% of MMT. The
nanocomposites were well dispersed and showed enhanced thermal stability, an increase
in Tg by 6°C, and slightly higher molecular weight than pure PMMA. Huang and Brittain
developed PMMA nanocomposite using 5 wt.% of MMT and a polymerizable surfactant, [2-(methacryloyloxy)ethyl] trimethylammonium chloride, via emulsion polymerization at 80°C for 12 hours. The morphology appeared to be exfoliated by XRD but no TEM evidence was presented. Thermal degradation for 20 wt.% loss was enhanced significantly up to 341°C, \( T_g \) increased by 15°C over the pure polymer, and molecular weight increased to 565,000 for the nanocomposite.

Meneghetti and Qutubuddin [61, 62] synthesized PMMA-clay nanocomposites via both \textit{in situ} and emulsion polymerization techniques with MMT and a zwitterionic surfactant, octadecyl dimethyl betaine (C18DMB). Partial exfoliation was achieved with significant improvement in \( T_g \) by 18°C for the emulsion product over pure PMMA [62]. Intercalated nanocomposite from \textit{in situ} polymerization had a \( T_g \) 10° lower than the emulsion product. The storage modulus of partially exfoliated nanocomposite was superior to the intercalated structure at higher temperatures and to the pure polymer. The rubbery plateau modulus was over 30 times higher for the emulsion product versus pure PMMA as shown in Figure 1.4. Emulsion technique produced nanocomposites of highest molecular weight (930,000) with bimodal distribution reported in the literature.
1.4.3 Rubber Clay Nanocomposites

The field of nanocomposites has extended to elastomeric matrices, particularly, for potential applications where enhanced barrier properties are desired. Styrene-butadiene rubber (SBR) is a commodity elastomer due to its high volume production and its low market price. SBR-clay nanocomposites have been synthesized, in most cases, by mixing the organoclay in an industrial mixer (2-roll mill and/or Brabender mixer) followed by vulcanization [63-70]. Mousa and Karger-Kocsis [63] reported an increase in tensile strength by 5 times with 10 phr (parts per hundred rubber) of clay content. Ganter et al. [66, 67] prepared intercalated and partially exfoliated SBR-clay nanocomposites with 30 phr organoclay as verified by TEM. The authors also prepared samples using solvent, where the organoclay is dispersed in toluene, and mixed with a toluene-rubber solution for 24 hours followed by solvent removal. Solvent mixed systems demonstrated
higher clay dispersion. Figure 1.5 [66] shows the tensile strength and strain of SBR-clay nanocomposites and also for precipitated silica (3370) filled systems; organoclay system demonstrated higher strength than silica. The mechanical reinforcement and hysteresis are related to the anisotropic nature of the clay aggregates and concomitant orientation during strain [67]. Due to anisotropic structure of the clay, Schon and Gronski [69] observed that the percolation threshold is much lower for the organoclay system versus silica filled SBR. The gas barrier property was not reported.

![Figure 1.5. Tensile strength and strain at break for SBR and SBR nanocomposites filled with organoclay or precipitated silica (3370); TESPT is a coupling agent and swelling indicates that solvent was used during mixing [66].](image)

Another commodity rubber used in nanocomposites is natural rubber (NR) [71-76]. NR-clay nanocomposites have shown significant improvement in mechanical properties. Varghese and Karger-Kocsis [73] mixed NR latex with organoclay forming NR nanocomposites of high stiffness and low damping characteristics. Most of the NR nanocomposites however are derived from high molecular weight NR. NR-clay (10 phr) nanocomposite has also demonstrated comparable mechanical properties to NR filled
with 40 phr carbon black [71]. The clay improved the strength of NR without reducing the elasticity of the material.

Acrylonitrile-butadiene rubber, also known as nitrile or NBR, is a specialty rubber mostly used in automotive components (e.g. belts, O-rings). Toyota group synthesized intercalated NBR-clay nanocomposites (4% clay by volume) which had hydrogen and water vapor permeability 30% lower than pure rubber [77]. Similar barrier properties were also observed by Wu et al. [78]: with 10% clay by volume, nitrogen permeability decreased by almost 50%. Nanocomposites also showed enhanced tensile strength and modulus [79]. Nanocomposites from ethylene propylene diene methylene (EPDM), another specialty rubber, demonstrated improved barrier performance as well. Usuki and Tukigase [80] synthesized EPDM with 4% wt. organoclays which exhibited 30% decrease in permeability of nitrogen and 2 times higher tensile strength than pure EPDM.

1.5. SCOPE OF PRESENT WORK

This dissertation addresses both fundamentals of nanocomposite technology and applications to rubber. It is critical to select suitable surfactants to improve the affinity between rubber matrix and clay nanolayers. The work focused on (i) the synthesis and characterization of functionalized clay using specialty surfactants, and (ii) the development of intercalated or exfoliated rubber nanocomposites using functionalized clay. Suitable surfactants will enable nano-dispersion of clay in the rubber matrix and lead to desired improvements in barrier and also thermo-mechanical properties. Chapter 2 describes the synthesis of three specialty surfactants – vinylbenzyl-dodecyldimethylammonium chloride (VDAC), vinylbenzyloctadecyldimethylammonium chloride (VODAC), and octadecyldimethyl betaine (C18DMB) – and MMT modification
via ion exchange. A commercial surfactant, octadecylamine (C18amine), was used as well for comparison. In Chapter 3, SBR/clay nanocomposites were synthesized via mechanical mixing using with four different types of organoclays. The mechanical and barrier properties of these nanocomposites make them attractive for tire application. In Chapter 4, an attempt to model the permeability and the modulus of the nanocomposites as a function of clay loading was done. In Chapter 5, the effects of carbon black on SBR and on SBR/clay nanocomposites were investigated. In fact, the synergism of organoclays with carbon blacks can bring similar mechanical and barrier properties at a lower filler loading than carbon black alone at high concentration. In Chapter 6, two other types of rubber – natural rubber and bromo-butyl rubber – were used in the synthesis of rubber/clay nanocomposites. In Chapter 7, a different type of nanocomposite is described: PMMA/clay nanocomposite gel electrolyte for lithium battery application. The morphology and the effect of clay on the ionic conductivity and stability were analyzed. Finally, Chapter 8 summarizes the overall conclusions and suggests future work.

1.6. REFERENCES


CHAPTER 2
SYNTHESIS OF SPECIALTY SURFACTANTS AND ION EXCHANGED CLAYS

2.1 INTRODUCTION

The functionalization of clay by surfactants is a critical factor in the synthesis of polymer/clay nanocomposites. The clay, montmorillonite (MMT), which is originally hydrophilic, must become organophilic to be compatible with the monomer or polymer, in order to yield well dispersed silicates forming exfoliated polymer/clay nanocomposites. The functionalized clay should have strong interaction with a specific monomer or polymer, improving the interfacial adhesion between the organic and inorganic phases of the nanocomposite. In this thesis, one of the main objectives was to find a suitable surfactant to functionalize the clay for a specific polymer/clay nanocomposite system. In the particular case where styrene-butadiene rubber (SBR) is the matrix, four different surfactants were investigated in order to determine which surfactant-clay system provided the best performance of the nanocomposite.

The first surfactant investigated was octadecyldimethyl betaine (C18DMB), which was synthesized in the laboratory according to C.S. Lin’s Ph.D. thesis [1]. C18DMB is a zwitterionic surfactant with a chain length of 18 carbon atoms. The long chain length is attractive since it can increase considerably the d-spacing of the clay layers during the ion exchange. Functionalized MMT with C18DMB has successfully led to the synthesis of partially exfoliated poly(methyl methacrylate) (PMMA)/clay nanocomposites [2,3]. Two other similar surfactants developed in the laboratory by Fu [4,5] but with different chain lengths (12 or 18 carbon atoms) were also investigated:
vinylbenzyldodecyldimethylammonium chloride (VDAC) and vinylbenzyl-octadecyldimethylammonium chloride (VODAC), respectively. These are cationic surfactants polymerizable with styrene molecule. Fu [6] demonstrated that the styrenic group in the surfactant has very high affinity with styrene monomer and the long alkyl chains weaken the attraction between the clay nanolayers forming completely exfoliated polystyrene (PS)/clay nanocomposites. The strong interaction between the surfactant and the styrene molecule may also be important in the SBR system. Finally, a commercial cationic surfactant was used for comparison as well: octadecylamine (C18amine). With a chain length of 18 carbon atoms, it has been used with clay in many different nanocomposite systems.

In this chapter, the synthesis of the three laboratory-synthesized surfactants is described along with their NMR characterization. The functionalization of clay by the surfactants is studied as well via x-ray diffraction and thermogravimetric analysis. The arrangement of the surfactants inside the silicate layers is analyzed theoretically in terms of the number of surfactant molecules inside the clay gallery with a particular d-spacing.

2.2 EXPERIMENTAL

2.2.1 Materials

Sodium chloroacetate, provided by Aldrich, and octadecyl dimethyl amine, provided by Ethyl Corp., were reactants for the synthesis of the zwitterionic surfactant C18DMB. Also, 2-propanol and chloroform were used as solvents for the synthesis. Ethyl ether, dodecyl dimethyl amine (DDA), and vinylbenzyl chloride (VBC) (containing 500 ppm tert-butylcatechol and 500 ppm nitroparaffin inhibitors) were purchased from
Aldrich for the synthesis of VDAC and VODAC. Octadecylamine was supplied by Aldrich as well. MMT used in this study was provided by Southern Clay Products (under the trade name of Mineral Colloid BP) and contains exchangeable cations of primarily $\text{Na}^+$. Mineral Colloid BP is a fine powder with an average particle size of 75 $\mu\text{m}$ in the dry state, and a cation exchange capacity (CEC) of 90mEq/100g.

### 2.2.2 Synthesis of octadecyldimethyl betaine (C18DMB)

The chemical reaction involved in the synthesis of C18DMB is shown below:

$$\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3(\text{CH}_2)_{17}\text{N} + \text{ClCH}_2\text{COONa} & \quad \rightarrow \quad \text{CH}_3(\text{CH}_2)_{17}\text{N}^+\text{CH}_2\text{COO}^- + \text{NaCl} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}$$

A solution of 120 ml of distilled water containing 9.33 g of sodium chlororacetate was added dropwise to a magnetically stirred solution of 22.85 g of octadecyldimethyl amine dissolved in 63 ml of 2-propanol in a 250 ml round bottomed flask. The cloudy mixture was heated to 80°C and a clear solution was observed. This solution was further refluxed for 24 hours and then cooled to room temperature. This clear solution was distilled under reduced pressure at 80°C to remove most of the 2-propanol and water, and the solid wax was further dried at 80°C under reduced pressure overnight. The dried white solid was added to 50 ml of chloroform and magnetically stirred in a sealed 125 ml round bottomed flask at room temperature for 4 hours. The white precipitate (excess sodium chloroacetate and NaCl) was filtered off. The clear filtrate obtained, which
consisted of C18DMB in chloroform, was distilled and further dried at 80°C under reduced pressure overnight. A highly hygroscopic powder was obtained with 80% yield.

2.2.3 Synthesis of vinylbenzyldodecyldimethylammonium chloride (VDAC) and vinylbenzyloctadecyldimethylammonium chloride (VODAC)

The chemical reaction involved in the synthesis of VDAC and VODAC are shown below:

\[
\begin{align*}
\text{CH}_3
\end{align*}
\]
\[
\begin{align*}
| & |
\text{CH}_3(\text{CH}_2)_n\text{N} & + & \text{CH}_2=\text{CH-Ph-CH}_2\text{Cl} & \rightarrow & \text{CH}_3(\text{CH}_2)_n\text{N}^+\text{CH}_2-\text{Ph-CH=CH}_2 \\
| & |
\text{CH}_3
\end{align*}
\]

[n-alkyldimethyl amine] [vinylbenzyl chloride] [vinylbenzyl n-alkyldimethylammonium chloride]

Vinylbenzyl n-alkyldimethylammonium (n=12, 18) chlorides were synthesized by the reaction of vinylbenzyl chloride with the corresponding n-alkyldimethyamines (one half stoichiometric excess) in ethyl ether at room temperature for 24 hours. Then, the mixture was placed in the refrigerator for 48 hours. The precipitate was filtered and washed with ethyl ether and dried under vacuum. The product was a white powder with 70% yield for both VDAC and VODAC.

2.2.4 Ion exchanged clays (C18DMB-MMT, VDAC-MMT, VODAC-MMT, and C18amine-MMT)

Organophilic clays were prepared by ion exchange of Na⁺ with the organic ammonium salts: C18DMB, VDAC, VODAC, or C18amine. 10 g of MMT was suspended in 1 liter of distilled water and stirred for 30 minutes. An aqueous solution of
12 mmoles of a certain surfactant (in the case of C18DMB, solution contained also 1 mL of HCl (0.027 mole)) was added with continued stirring. After 30 minutes, approximately 2 ml of HCl was added to neutralize the mixture and then stirred for additional 3 hours. The solution was left idle overnight. The product was then filtered, washed several times with hot distilled water until no chloride was detected with 0.1 M AgNO₃ solution, and vacuum dried. The cation exchanged MMT was ground using a mortar and pestle, and particles with size less than 65 µm were collected. The modified clays are referred to as “C18DMB-MMT, or VDAC-MMT, or VODAC-MMT, or C18amine-MMT”.

2.2.5 Characterization

¹H-NMR spectra of the surfactants were obtained using a Varian XL-200 (200 MHz) spectrometer with CDCl₃ as the solvent. The spectra were referenced with the residual solvent peak (7.26 ppm). Their chemical shifts were reported as ppm values and compared to Lin’s and Fu’s results. X-ray diffraction (XRD) patterns of organoclays were obtained by using a Phillips XRG 3100 X-ray generator equipped with a Ni-filtered Cu-Kα (1.5418 Å) source that was connected to a Phillips APD 3520 type PW 1710 diffractometer controller. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA 2950. Samples of 10 to 15 mg were heated to 800°C at a rate of 20°C/min under nitrogen atmosphere. Fourier transform infrared (FTIR) absorption spectra were obtained with a BOMEM spectrometer in the range of 4000-500 cm⁻¹. A 45° prism was used to record the attenuated total reflectance (ATR).
2.3 RESULTS AND DISCUSSION

2.3.1 Surfactants

The synthesis of C18DMB resulted in a white powder with a yield of approximately 80%. The $^1$H-NMR spectrum showed in Figure 2.1 is in agreement with the results from Lin [1]. Table 2.1 presents each of the six chemical shifts. In the case of VDAC and VODAC, a white precipitate was formed after the synthesis, with a yield of 70%, and the $^1$H-NMR spectra, shown in Figure 2.2, were similar to the results obtained by Fu [6]. The chemical shifts are also reported in Table 2.1. Notice that C18DMB and VODAC have the same chain structure except for the carboxylic group and styrenic group, respectively.

Figure 2.1. $^1$H-NMR spectrum for octadecyldimethyl betaine (C18DMB) in CDCl3.
(VDAC: n = 9; VODAC: n = 15; C18DMB n = 15 and COO\(^-\) replaces vinylbenzyl group)

<table>
<thead>
<tr>
<th>Chemical Shifts (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
</tr>
<tr>
<td>VDAC</td>
</tr>
<tr>
<td>VODAC</td>
</tr>
<tr>
<td>C18DMB</td>
</tr>
</tbody>
</table>

Table 2.1. 1H-NMR spectral data of VDAC, VODAC, and C18DMB in CDCl\(_3\).

Figure 2.2.a. \(^1\)H-NMR spectrum for vinylbenzyldodecyldimethylammonium chloride (VDAC) in CDCl\(_3\).
2.3.2 Ion exchanged clays

The surfactants described in this chapter are used for ion exchange of Na$^+$ montmorillonite. The sodium ions are exchanged by cationic ions from the surfactants via the following mechanism described by Cowan and White [7]:

$$NaZ + RNH_3^+ \Leftrightarrow Na^+ + RNH_3Z$$

where Z is the montmorillonite and R is the alkyl chain of the surfactant. The surface of the clay becomes organophilic, opposite of its pure state, hydrophilic.

X-ray diffraction (XRD) is a common technique used in examining surfactant intercalation and expansion of MMT [8, 9]. As MMT interlayer spacing can expand or contract, the d$_{001}$ reflection of XRD will shift proportionally. The d$_{001}$ spacing was calculated from the XRD peak position using Bragg’s law:

Figure 2.2.b. $^1$H-NMR spectrum for vinylbenzyloctadecyldimethylammonium chloride (VODAC) in CDCl$_3$. 

54
\[ d = \frac{\lambda}{2 \sin \theta} \]  

where \( d \) is the \( d_{001} \) spacing, \( \lambda \) is the x-ray wavelength equal to 1.5418 Å, and \( \theta \) is the incidence angle of x-ray. Figure 2.3 shows the XRD patterns of untreated MMT and C18DMB-MMT. The unmodified clay, after vacuum drying, has an interlayer spacing of approximately 1.04 nm. In the case of C18DMB-MMT, the organic cations penetrate into the interlayer space, replacing the sodium cations and the peak position shifts to a lower angle corresponding to 2.24 nm. The shoulder around 3° (2\( \theta \)) indicates that some C18DMB molecules are broadly distributed, allowing for slightly higher \( d \)-spacing than 2.24 nm. XRD curves for the other organoclays are illustrated in Figure 2.4. VODAC-MMT has the highest \( d_{001} \) spacing of 2.32 nm, C18amine-MMT \( d_{001} \) is 2.24 nm, and VDAC-MMT \( d_{001} \) is 2.04 nm. The increment of intergallery spacing is roughly proportional to the alkyl chain length of the surfactants.

Figure 2.3. XRD patterns of unmodified MMT and C18DMB-MMT.
Figure 2.4. XRD patterns of VODAC-MMT, C18amine-MMT and VDAC-MMT.

For further evidence of intercalation, in particular the amount of surfactant present in the clay galleries, TGA measurements were performed on the organoclays. TGA curves are shown in Figure 2.5. The curve for untreated MMT indicated a 5 wt.% loss while heating the material to 800°C. The first part of the weight loss, between 50° and 200°C is from the adsorbed water in the interlayer gallery. The weight loss between 400° and 700°C corresponds to the loss of the OH groups and the collapse of the crystallographic structure. In the case of the organoclays, besides the decomposition due to loss of water and OH groups, there is also a loss due to degradation of the surfactant in the clay interlayer at temperatures between 200° and 700°C. The observed weight loss for
C18DMB-MMT, VODAC-MMT, VDAC-MMT, and C18amine-MMT determined from the TGA due to the intercalated surfactant are 29, 28, 27, and 26 wt.%, respectively.

![TGA thermograms of weight loss as a function of temperature for Na-MMT, C18DMB-MMT, VODAC-MMT, VDAC-MMT, and C18amine-MMT](image)

Figure 2.5. TGA thermograms of weight loss as a function of temperature for Na-MMT, C18DMB-MMT, VODAC-MMT, VDAC-MMT, and C18amine-MMT

### 2.3.3 Surfactant arrangement inside the clay

The arrangement and orientation of the surfactant chains inside the clay layers is commonly derived from the XRD results. According to Lagaly [10], depending of the d-spacing obtained from XRD, the alkyl chains can be oriented parallel to the clay layers as a monolayer or bilayer or, in some cases as tilted monolayer or bilayer. However, these arrangements assume fully extended chains with *all-trans* segments. Vaia et al. [11] reported that this can be misleading since aliphatic chains can assume a variety of configurations because of the relative small energy difference between *trans* and *gauche*
conformers (0.6 kcal/mol). Hackett et al. [12] used molecular dynamics simulation along with FTIR to determine that the alkyl ammonium surfactants do not lie completely straight inside the layers. The frequency of CH$_2$ infrared adsorption band is sensitive to gauche/trans conformer ratio of the chains, and can be used to determine the structural arrangement of the surfactants. Even with these latest findings, the surfactant arrangements inside the clay layers are not well characterized and understood. Thus, an attempt is made to characterize the surfactant chain orientation in the organoclays.

Montmorillonite has an overall surface area of 750 m$^2$/g [13] and its cation exchange capacity is 90 mEq/100g, from which the total moles of surfactant that participate in 100% ion exchange can be calculated. The layer area per molecule available in MMT is then 0.68 nm$^2$. This value is important when the packing of the chains is considered: the cross sectional area of the surfactant must be within this limit. This area can be determined by using the software Chem 3D Pro and assuming a straight chain molecule. In the case of the surfactant being tilted, the cross sectional area calculated is the projected area into the plane of the clay surface. Table 2.2 presents the XRD and FTIR data as well as the calculated cross sectional areas for the most favorable orientation of each surfactant. As was mentioned before, VODAC-MMT has the highest gallery height in comparison with the other organoclays. The FTIR measurements focus on the band around 2920 cm$^{-1}$ arising from CH$_2$ asymmetric stretch, $\nu_{as}$(CH$_2$). This band shifts from lower frequencies (characteristic of highly ordered all-trans conformations) to higher frequencies as the number of gauche conformations along the hydrocarbon chain increases [14]. VDAC is the most disordered chain in comparison to C18DMB and
VODAC. Similar results were obtained by Vaia et al. [11] where the shortest surfactant chains showed highest disorder.

<table>
<thead>
<tr>
<th>Gallery height (nm) (^a)</th>
<th>VDAC-MMT</th>
<th>VODAC-MMT</th>
<th>C18amine-MMT</th>
<th>C18DMB-MMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>2929.4</td>
<td>2922.2</td>
<td>2920.0</td>
<td>2917.6</td>
<td></td>
</tr>
<tr>
<td>ν(_{as}) \text{CH}_2 (\text{cm}^{-1})</td>
<td>0.68</td>
<td>0.68</td>
<td>0.68</td>
<td>0.68</td>
</tr>
<tr>
<td>Layer area / molecule (nm(^2))</td>
<td>42</td>
<td>30</td>
<td>29</td>
<td>27</td>
</tr>
<tr>
<td>Surfactant orientation (degrees)</td>
<td>0.39</td>
<td>0.79</td>
<td>0.75</td>
<td>0.81</td>
</tr>
</tbody>
</table>

\(^a\) \(d_{001} = 1.04\) nm (from NaMMT)

\(^b\) cross sectional area projected from angle of orientation

Table 2.2. Summary of XRD and FTIR data, cross sectional area and orientation of surfactant molecule for organophilic clays.

Therefore, from the gallery height and the available surface area available, the following configurations were determined: tilted monolayers at angles of 42, 30, 29 and 27 for VDAC, VODAC, C18amine, and C18DMB, respectively. The cross sectional areas projected for each orientation are displayed in Table 2.2. VDAC is the only system where the cross sectional area was much smaller than the available clay surface area; the chains are able to adopt a more disordered structure. In the case of VODAC, the molecule is straighter than VDAC and tilted around 30°; the chains are more densely packed and the interlayer spacing is the highest among all organoclays. For C18amine and C18DMB, the chains are tilted at a lower angle due to the lower d-spacing; the straight chains with mostly \(trans\) conformations are very densely packed. Figure 2.6 shows a schematic representation of the different surfactants on MMT.
2.4 SUMMARY

A zwitterionic surfactant, C18DMB, was synthesized along with two cationic surfactants, VDAC and VODAC, (same functional group but different chain lengths) for use in the functionalization of montmorillonite. Ion exchange of sodium ion with the cationic ions from the surfactants increased the d-spacing of the clay as verified by XRD. The increase is as much as 1.28 nm for VODAC. The surfactant orientation and arrangement were calculated; monolayers of surfactants are tilted in a certain angle to accommodate the packing area and the gallery height available. Based on FTIR measurements on the band around 2920 cm$^{-1}$ (CH$_2$ asymmetric stretch) the chains in VDAC are less oriented than in C18DMB, C18amine, and VODAC.

2.5 REFERENCES


CHAPTER 3
SYNTHESIS AND CHARACTERIZATION OF SBR-CLAY NANOCOMPOSITES

3.1. INTRODUCTION

Polymer nanocomposites have been intensely researched in the last decade since the addition of a small quantity of reinforcement fillers (up to 10 wt.%) such as clays in the polymer matrix have led to improvements of mechanical, thermal, and barrier properties [1-4]. The enhancement of such properties is strongly influenced by the nanostructure of the dispersed clay and by its interfacial interaction with the polymer. Montmorillonite (MMT) is a smectite type clay commonly used, and has an octahedral aluminate sheet sandwiched between two tetrahedral silicate layers. The original montmorillonite is hydrophilic; however, the sodium cations can be ion-exchanged for organic cations from surfactants, especially with alkylammonium ions [5]. The clay becomes organophilic and more compatible with polymer [6, 7].

The application of organophilic clay in elastomers can also provide a new technology of rubber/clay nanocomposites with enhanced properties. Kojima et al. [8] synthesized intercalated acrylonitrile-butadiene rubber (NBR)-clay nanocomposites (4% clay by volume) and proposed that these nanocomposites can be used as tire innerliners due to their significantly reduced gas permeability. Nanocomposite research in rubbers has been very limited. The effect of clay on permeability for other rubbers such as styrene-butadiene rubber (SBR) has not been reported yet.

SBR-clay nanocomposites have been synthesized, in most cases, by mixing the organoclay in a industrial mixer (2-roll mill and/or Brabender mixer) followed by vulcanization [9-16]. Some of these reports have also used solution mixing to enhance the
disruption of the clay particles [11-13, 16]. Mousa and Karger-Kocsis [9] reported an increase in tensile strength by 5 times to a value of 15 MPa with 10 phr (parts per hundred rubber) of clay content. Wang and coworkers [10, 11] also prepared nanocomposites with higher mechanical properties than SBR via melt intercalation of raw rubber in a mixer or by mixing latex SBR with organoclay. For instance, the tensile strength of nanocomposite via latex method had tensile strength of 12.4 MPa with 30 phr organoclay [11]. Ganter et al. [12, 13] prepared intercalated SBR-clay nanocomposites with some partially exfoliated silicates indicated by TEM for sample containing 30 phr organoclay. X-ray diffraction was not used to characterize the morphology. The authors also demonstrated enhanced clay dispersion using a solvent mixing technique, where the organoclay is dispersed in toluene, mixed with a toluene rubber solution for 24 hours followed by solvent removal. However, the tensile strength was not as high (10 MPa) as for the samples prepared without the solvent (12 MPa) [12]. Schon and Gronski [15] compared the mechanical properties of silica filled versus clay filled composites. Clay filled systems presented greater tensile strength and modulus than silica composites; the percolation threshold was much lower for the organoclay system due to anisotropic structure of the clay. Sadhu and Bhowmick [16] synthesized exfoliated SBR/clay nanocomposite using solution mixing prior to vulcanization. Different surfactants with chain lengths ranging form 10 to 18 carbons were used, with the best results for surfactant with the longest chain length: tensile strength increased up to 3 times to 3.4 MPa for samples with 16 wt.% organoclay compared to pure SBR.

This chapter describes the synthesis of SBR/clay nanocomposites via mechanical mixing with four different types of organoclays. The effects of using different surfactant
chain lengths and different functional groups to modify montmorillonite for SBR nanocomposites are investigated. The morphology of the nano-layers in the rubber matrix is affected by the surfactant type. Mechanical and barrier properties of nanocomposites showed significant improvements versus pure SBR or SBR with unmodified clay.

3.2. EXPERIMENTAL

3.2.1 Materials

The elastomer used for preparing nanocomposites was SBR (Nipol 1502; Mooney viscosity according to ML (1+4) at 100°C = 52; styrene content 23 wt.%; random copolymer) supplied by the Zeon Corporation. Mooney viscosity is a widely used notation to characterize rubber; it is recorded with a rotational viscometer with a large rotor if the term “ML” is indicated. The terms “1” and “4” represent the preheat time (minutes) before the rotor starts to turn, and the time of actual rotation of the rotor before the final Mooney viscosity measurement is made, respectively. MMT used in this study was provided by Southern Clay Products (under the trade name of Mineral Colloid BP) and contains exchangeable cations of primarily Na⁺. Mineral Colloid BP is a fine powder with an average particle size of 75 µm in the dry state, and a cation exchange capacity (CEC) of 90mEq/100g. The following surfactants used to ion exchange the clay were synthesized in the laboratory as described in chapter two: vinylbenzyl octadecyldimethyl ammonium chloride (VODAC) [17], vinylbenzyl dodecyldimethyl ammonium chloride (VDAC) [18] and octadecyldimethyl betaine (C18DMB) [19]. The ion exchange process was also described in Chapter 2. Octadecylamine was purchased from Aldrich. The ingredients used during the rubber processing such as zinc oxide, stearic acid, and sulfur
were supplied by Harwick Standard, agerite stalite and copper dimethylthiocarbamate (cummate) by R.T. Vanderbilt, and benzoathiazyl disulfide (MBTS) by AkroChem. Zinc oxide and stearic acid react with the accelerator enabling it to exert its full function. Agerite stalite is used as an antioxidant. Sulfur is used exclusively for vulcanization. MBTS is the accelerator most extensively used today for vulcanization of SBR and cummate is an ultra-accelerator used at small quantity with MBTS.

3.2.2 Processing

SBR/clay nanocomposites were prepared by mixing the rubber, zinc oxide (5 phr), stearic acid (2 phr), agerite stalite (1 phr), and clay in a Brabender mixer (Plasti-Corder PL 2000) for 10 minutes at 80°C. The compound was then milled in a 2-roll mill (Farrel) at room temperature with the vulcanizing agents: sulfur (2 phr), MBTS (1.5 phr), and cummate (0.1 phr). The vulcanization was achieved by compression molding at 160°C for 20 minutes. The samples prepared are listed in Table 3.1, which also gives the weight and volume fraction of the inorganic filler. The density of MMT is 2.6 g/cm³. The organoclayls contain roughly 15 to 30 wt.% of surfactant (depending on the molecular weight of each surfactant), but the volume and weight fraction in Table 3.1 account for only the silicate content in order to compare the nanocomposites with similar inorganic material. The total weight and volume fractions for the various surfactant treated clays are given in Table 3.2.
**Table 3.1.** Samples prepared for SBR/clay nanocomposites and their respective silicate weight and volume fraction.

<table>
<thead>
<tr>
<th>Clay Type</th>
<th>VODAC-MMT</th>
<th>VDAC-MMT</th>
<th>C18DMB-MMT</th>
<th>C18amine-MMT</th>
<th>Na-MMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.031</td>
<td>0.012</td>
<td>0.032</td>
<td>0.013</td>
<td>0.032</td>
</tr>
<tr>
<td>10</td>
<td>0.059</td>
<td>0.023</td>
<td>0.062</td>
<td>0.024</td>
<td>0.062</td>
</tr>
<tr>
<td>20</td>
<td>0.108</td>
<td>0.044</td>
<td>0.114</td>
<td>0.047</td>
<td>0.115</td>
</tr>
<tr>
<td>30</td>
<td>0.151</td>
<td>0.063</td>
<td>0.159</td>
<td>0.067</td>
<td>0.161</td>
</tr>
</tbody>
</table>

**Table 3.2.** Samples prepared for SBR/clay nanocomposites and their total organoclay weight and volume fraction.

<table>
<thead>
<tr>
<th>Modified Clay Type and Content</th>
<th>VODAC-MMT</th>
<th>VDAC-MMT</th>
<th>C18DMB-MMT</th>
<th>C18amine-MMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.043</td>
<td>0.026</td>
<td>0.043</td>
<td>0.024</td>
</tr>
<tr>
<td>10</td>
<td>0.082</td>
<td>0.050</td>
<td>0.082</td>
<td>0.048</td>
</tr>
<tr>
<td>20</td>
<td>0.152</td>
<td>0.095</td>
<td>0.152</td>
<td>0.091</td>
</tr>
<tr>
<td>30</td>
<td>0.212</td>
<td>0.137</td>
<td>0.212</td>
<td>0.131</td>
</tr>
</tbody>
</table>

**3.2.3 Characterization**

X-ray diffraction (XRD) measurements were made using a Rigaku RINT 2000 wide angle x-ray diffractometer (40kV, 40 mA) equipped with a Ni-filtered Cu-Kα (1.5418 Å) source. Transmission Electron Microscopy (JEOL 1200 EX TEM) operated at 80 kV was used to investigate the nano-structure of SBR/clay nanocomposites. The ultrathin sections with a thickness of 100 nm were microtomed at -80°C using a MT-7000 ultramicrotome. The direction of the compression mold relative to the TEM samples surface was perpendicular. Oxygen flux, $J(t)$, at 25ºC, 0% relative humidity and 1 atm pressure were measured with a OX-TRAN® 2/20 (MOCON) unit, which employs a
continuous-flow cell method approved by ASTM (Designation: D 3985-81). Tensile strength and strain tests were carried out according to ISO 37 using a Shimazu Autograph ABS-1000 at crosshead speed of 50 cm/min. The average of three tests is reported here.

The hardness was measured according to ISO 48 using a type A Durometer. The tensile strength, strain, and hardness measurements were provided by Yokohama Rubber Company (YRC). Dynamic mechanical properties were measured using a Dynamic Mechanical Thermal Analyzer (DMTA) from Rheometric Scientific. The samples (0.5 x 10 x 25 mm³) were swept at 3°C min⁻¹ from -90°C to 80°C at a frequency of 1 Hz. The storage modulus (E′), the loss modulus (E″) and mechanical loss factor (tan δ) were determined. Differential scanning calorimetry (DSC) was performed on a TA Instrument DSC 550 from -110°C to 20°C at a heating rate of 10°C/min.

3.3 RESULTS AND DISCUSSION

3.3.1 Morphology

SBR/clay nanocomposites were analyzed by X-ray diffraction to verify the changes in the clay galleries due to intercalation and exfoliation. Figure 3.1 shows XRD of nanocomposites with 10 phr of clay (C18DMB-, C18amine-, VODAC-, VDAC-, and Na-MMT). Intercalation was clearly observed for samples with C18DMB, C18amine, VODAC, and VDAC since the d-spacings are higher than for organoclays (Figures 2.3 and 2.4). In the case for VODAC-MMT, one sharp peak was observed indicating d-spacing of 3.15 nm and two smaller peaks corresponding to 1.73 nm and 1.2 nm. The first peak corresponds to intercalated SBR. The second and third peaks represent the collapse (reduction in d-spacing) of the clay layers as previously reported by Varghese et al. [20,
21] for natural rubber and epoxidized natural rubber nanocomposites. In the case of natural rubber containing montmorillonite treated with C18amine, XRD indicated a second and third peak at 1.68 and 1.24 nm, respectively [21]. This behavior was hypothetically due to interactions of the surfactant with vulcanizing agents which led to the removal of the surfactant from the interlayers of the silicate causing a decrease in the d-spacing. In accelerated sulfur curing process in the presence of zinc, the zinc is prone to coordination complexing in which amine groups present in the surfactant and sulfur of the sulfuric curatives may participate [21, 22].

Figure 3.1. XRD of cured SBR nanocomposites with 10 phr of VDAC-, VODAC-, C18DMB-, C18amine-, and Na-MMT.
In the case of C18DMB-MMT, at least three peaks were detected: 3.84 and 2.76 nm corresponding to intercalated SBR, and 1.77 nm corresponding to the collapsed clay layers. For SBR/C18amine-MMT, one sharp peak was observed indicating rubber intercalation (2.94 nm) and a small peak indicating collapsed clay layers (1.63 nm). The 2.94 nm d-spacing was the smallest among the 18 carbon chain surfactants (C18DMB, VODAC, and C18amine) since C18amine is a straight chain molecule without any functional group to strengthen the clay compatibility with the rubber. For SBR/VDAC-MMT, XRD indicated one peak corresponding to 3.15 nm, similar to VODAC. A second broad peak, 1.6 nm, corresponding to the collapsed structure with similar intensity as the first peak was also observed. The styrenic functional group favors intercalation as was observed for VODAC and VDAC nanocomposites; however, the shorter chain length in VDAC (12 carbons) reduces the availability of this functional group to interact with SBR in comparison to VODAC (d-spacing of VDAC-MMT is 0.28 nm smaller than VODAC-MMT from Figure 2.4). Thus, the amount of intercalation is smaller for SBR/VDAC-MMT. The ratio of intercalation and collapsed structure (from XRD) are equivalent and the TEM micrographs, discussed later, will show a large quantity of tactoids/aggregates in SBR/VDAC-MMT. For SBR filled with untreated MMT, slight intercalation of rubber occurred as the d-spacing of clay increased to 1.2 nm.

For nanocomposites at higher organoclay concentration, the dispersed silicates had slightly lower d-spacing. For instance, in the case of SBR/VODAC-MMT shown in Figure 3.2, the d-spacing of the main peak (3.15 nm) at 10 phr decreased to 3.04 and 2.76 nm at 20 and 30 phr, respectively. Steric hindrance of the silicates at high concentration decreases the expansion of the layers.
Figure 3.2. XRD of cured SBR nanocomposites at 10, 20 and 30 phr of VODAC-MMT.

The x-ray diffraction of uncured systems (Figure 3.3) did not show any peaks. For uncured sample with VODAC-MMT, the clay must be well dispersed and system is either fully exfoliated or contains clay layers at higher d-spacing than the cure system. There is no indication of collapsed layers which is in agreement with Varghese and Karger-Kocsis [21] hypothesis since in the uncured system complexing have not begun. After vulcanization, hot pressing as well as amine complexing reduce the d-spacing of the clay layers.
Figure 3.3. XRD of uncured SBR and SBR/VODAC-MMT.

TEM was used in order to visualize the morphology of the clay layers in the nanocomposites. Figure 3.4 shows TEM micrographs for samples with 5 phr organoclay. Even though, x-ray diffraction indicated all intercalated structures, partially exfoliated layers can also be observed in the TEM pictures. In sample with VODAC-MMT (Fig. 3.4.a), the dispersion of the silicate nanolayers is more exfoliated than for the other two systems with C18DMB or VDAC (Figs 3.4b, and 3.4c). At higher concentrations similar observations were made: Figure 3.5 illustrates the TEM micrographs for 10 phr organoclays while Figure 3.6 depicts the TEM of SBR nanocomposite containing 20 and 30 phr VODAC-MMT. For SBR containing C18DMB-MMT and C18amine-MMT the clay dispersion is similar showing both intercalated and some partially-exfoliated layers. In the case of VODAC-MMT, the nano-dispersion is better; the clay sheets appear more
individually spaced and with less intercalated sheets than in C18amine or C18DMB. Even at high concentrations, the VODAC-MMT layers are well dispersed. For SBR/VDAC-MMT, however, large tactoids are present indicating poor dispersion.

![Figure 3.4. TEM micrographs of SBR + 5 phr VODAC-MMT (a), C18DMB-MMT (b), and VDAC-MMT (c).](image)

Figure 3.4. TEM micrographs of SBR + 5 phr VODAC-MMT (a), C18DMB-MMT (b), and VDAC-MMT (c).
Figure 3.5. TEM micrographs of SBR + 10 phr VODAC-MMT (a), C18DMB-MMT (b), C18amine-MMT (c), and VDAC-MMT (d).

Figure 3.6. TEM micrographs of SBR/VODAC-MMT at 20 phr (a) and 30 phr (b) treated clay.
The TEM micrographs were analyzed using *ImagePro* software to obtain the characteristic dimensions (length, width and aspect ratio) of the dispersed clay sheets. The clay layers were traced and their respective length and width were measured. The calculated values are reported in Tables 3.3-3.5 for different clay contents: (5, 10 and 20 phr). The type of surfactant used to modify the clay has a significant effect on the nanodispersion and aspect ratio of the silicates. Also, with increasing concentration, the layers appear longer and wider because the silicates are closer to one another (almost touching) in the lateral and vertical direction. The aspect ratio calculated, however, is similar. In some cases, the error for estimating the length and width of the clay sheets can be large because at higher concentrations it is more difficult to distinguish individual layers, and also because of the unclear focus in some spots of the micrographs.

<table>
<thead>
<tr>
<th>SBR + 5 phr</th>
<th>VODAC-MMT</th>
<th>C18DMB-MMT</th>
<th>VDAC-MMT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>std. dev.</td>
<td>std. dev.</td>
<td>std. dev.</td>
</tr>
<tr>
<td><strong>Length (nm)</strong></td>
<td>249</td>
<td>53</td>
<td>314</td>
</tr>
<tr>
<td><strong>Width (nm)</strong></td>
<td>12.5</td>
<td>3</td>
<td>26</td>
</tr>
<tr>
<td><strong>Aspect Ratio</strong></td>
<td>20</td>
<td>7</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 3.3. Estimated length, width, and aspect ratio of clay sheet for SBR/clay nanocomposites (5 phr filler)

<table>
<thead>
<tr>
<th>SBR + 10 phr</th>
<th>VODAC-MMT</th>
<th>C18amine-MMT</th>
<th>C18DMB-MMT</th>
<th>VDAC-MMT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>std. dev.</td>
<td>std. dev.</td>
<td>std. dev.</td>
<td>std. dev.</td>
</tr>
<tr>
<td><strong>Length (nm)</strong></td>
<td>505</td>
<td>129</td>
<td>364</td>
<td>54</td>
</tr>
<tr>
<td><strong>Width (nm)</strong></td>
<td>27</td>
<td>11</td>
<td>29</td>
<td>5</td>
</tr>
<tr>
<td><strong>Aspect Ratio</strong></td>
<td>19</td>
<td>11</td>
<td>13</td>
<td>11</td>
</tr>
</tbody>
</table>

Table 3.4. Estimated length, width, and aspect ratio of clay sheet for SBR/clay nanocomposites (10 phr filler).
Table 3.5. Estimated length, width, and aspect ratio of clay sheet for SBR/clay nanocomposites (20 phr filler).

<table>
<thead>
<tr>
<th>SBR + 20 phr</th>
<th>VODAC-MMT</th>
<th>C18amine-MMT</th>
<th>VDAC-MMT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>std. dev.</td>
<td>std. dev.</td>
<td>std. dev.</td>
</tr>
<tr>
<td>Length (nm)</td>
<td>576</td>
<td>264</td>
<td>300</td>
</tr>
<tr>
<td>Width (nm)</td>
<td>28</td>
<td>21</td>
<td>17</td>
</tr>
<tr>
<td>Aspect Ratio</td>
<td>23</td>
<td>8</td>
<td>19</td>
</tr>
</tbody>
</table>

The aspect ratio determined from TEM for SBR/VODAC-MMT was the highest in comparison to other rubber nanocomposites: 20, 19, and 23 for 5, 10, and 20 phr organoclay content, respectively. The partially-exfoliated silicate layers were well dispersed in the matrix due to the VODAC surfactant which has a long chain (18 carbons) and the styrenic functional group providing strong interactions among the rubber, surfactant, and clay. The surfactant makes the clay very compatible with SBR; it is possible that the styryl group is reacting with the carbon double bond present in SBR. In the case of SBR/C18amine-MMT, the surfactant is a straight chain (18 carbons) amine molecule without a functional group. The interactions among rubber, surfactant and clay are lower than with VODAC-MMT and clay dispersion resulted in aspect ratios of 13 and 19 with 10 and 20 phr C18amine-MMT content, respectively. For SBR/C18DMB-MMT, the dispersed layered silicates had aspect ratios lower than in the previous systems: 12 and 8 with 5 and 10 phr organoclay, respectively. C18DMB has an 18-carbon chain with a carboxylic functional group. When this surfactant was used in polystyrene/clay nanocomposite, intercalated morphology was observed [23]. Thus, the clay/surfactant interactions with styrene-butadiene rubber resulted in mostly intercalated structure with low aspect ratio. Finally, for SBR/VDAC-MMT, the layered silicates were intercalated and with the lowest aspect ratio among all rubber/clay nanocomposites studied: 11, 5, and
4 with 5, 10, and 20 phr VDAC-MMT, respectively. The short chain (12 carbons) reduces the d-spacing of the organoclay, and the availability of the styryl functional group which diminishes the interaction between clay and SBR, resulting in poor clay dispersion. The next sections will reveal the significant effect of surfactant type on the mechanical, thermal, and barrier properties of SBR/clay nanocomposites.

3.3.2 Mechanical Properties

SBR/clay nanocomposites showed significant improvements in stress-strain properties presented in Table 3.6. SBR/VODAC-MMT demonstrated greatest increase in modulus at 200%, 300%, and 400% elongation as a function of clay content when compared with other organoclay systems (Figure 3.7). This trend is also observed for the storage modulus of these rubber nanocomposites, which will be discussed later. In the case of SBR/VDAC-MMT, at low concentration (5 and 10 phr) the modulus was comparable to that of VODAC and C18amine, but at 30 phr the VDAC tactoids are much larger (lowest aspect ratio) and the modulus is not as high as for the longer surfactants. SBR/C18amine-MMT had a slightly higher modulus than SBR/C18DMB-MMT; in this case the clay dispersion is a factor, since nanocomposite with C18amine-MMT had higher aspect ratio than with C18DMB-MMT. SBR containing untreated Na-MMT showed very poor modulus enhancement as a function of clay.
Table 3.6. Mechanical properties of SBR/clay nanocomposites.
Elongation at break was drastically superior for SBR/clay nanocomposites than pure rubber shown in Figure 3.8. As the clay content increases, the elongation appears to reach a plateau around 30 phr clay. The fact that SBR/VODAC-MMT has a lower strain than other organoclays at 30 phr can be an indication that there is a strong matrix-clay interaction; that is VODAC is chemically bonded with SBR. This behavior of decrease in strain at break was observed when a reactive (matrix-filler) coupling agent such as bis(triethoxysilylpropyl-) tetrasulfan (TESPT) is used in presence of SBR/organoclay, since the chemical bond of the matrix to the filler reduces chain slipping along the filler surface [12].

Figure 3.8. Elongation at break for SBR nanocomposites versus clay content.
Tensile strength at break was enhanced tremendously for SBR/clay nanocomposites in comparison to the pure rubber and untreaded clay, as shown in Figure 3.9. In particular, VODAC-MMT and C18amine-MMT systems experienced highest tensile strength followed by C18DMB-MMT and VDAC-MMT, with the exception at 30 phr, where C18DMB-MMT was slightly stronger than VODAC-MMT and C18amine-MMT. These results also demonstrated the best reinforcements for SBR/organoclay nanocomposites (tensile strength of 18 MPa or higher for 30 phr organoclay treated with long chain surfactant) in comparison to literature reports on tensile strength at the break [10-13, 15, 16]. For instance, Schon and Gronski [15] prepared intercalated and partially exfoliated SBR nanocomposite containing 30 phr commercial organoclay (Nanomer I.42E) with tensile strength of approximately 14 MPa. The only discrepancy in our data is for SBR/C18DMB-MMT at low concentration (3 to 7 phr) where the tensile strength in Figure 3.9 is lower than SBR. These values are probably outliers or just bad specimens since the modulus and the storage modulus discussed later have reasonable values. Overall, it is very noticeable that organoclays reinforce SBR, while untreated Na-MMT actually decreases the rubber strength. The decrease in tensile strength with addition of untreated clay, at lower concentration, was observed also in natural rubber [24].
Finally, the hardness of SBR/clay nanocomposites was much superior to the pure rubber as shown in Figure 3.10. SBR/VODAC-MMT presented highest hardness (69 at 30 phr clay), followed by nanocomposites with C18amine-, C18DMB-, and VDAC-MMT. This data is also slightly superior to literature report: Wang and coworkers [11] prepared rubber clay nanocomposites with slightly lower hardness (68 at 30 phr) than for VODAC-MMT.
The storage modulus of the nanocomposites was measured with a Dynamic Mechanical Thermal Analyzer (DMTA) from -90°C to 80°C. At room temperature (25°C), sample with 10 phr VODAC-MMT presented a rubbery plateau three times larger than plain rubber and showed the highest increase among all nanocomposites as presented in Table 3.7. This increase in modulus was followed by samples with C18amine-MMT, C18DMB-MMT, and VDAC-MMT. This trend was also observed for the hardness and modulus of these nanocomposites as well as for the barrier property which will be discussed in the next section. Figure 3.11 illustrates the relative modulus as a function of volume fraction of montmorillonite silicate (a) or as a function of volume fraction of organoclay (b) for the different SBR nanocomposites. The sample with VODAC-MMT shows highest increase in modulus up to 30 phr (or 0.063 volume fraction).
fraction), followed by C18amine-MMT, C18DMB-MMT, and VDAC-MMT. Such tremendous reinforcement with VODAC-MMT is due to its nano-dispersion and possible reactivity with SBR. For SBR/VDAC-MMT, the modulus is lower because the shorter chain (12 carbons) reduces the availability of the styrenic functional group.

<table>
<thead>
<tr>
<th></th>
<th>Storage Modulus (Pa), 25°C</th>
<th>Tg, °C (DMTA)</th>
<th>Tg, °C (DSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>4.0 x 10⁶</td>
<td>-36.5</td>
<td>-44.1</td>
</tr>
<tr>
<td>SBR + 10 phr VODAC-MMT</td>
<td>1.2 x 10⁷</td>
<td>-37.5</td>
<td>-45.0</td>
</tr>
<tr>
<td>SBR + 10 phr C18DMB-MMT</td>
<td>6.9 x 10⁶</td>
<td>-35.5</td>
<td>-44.1</td>
</tr>
<tr>
<td>SBR + 10 phr VDAC-MMT</td>
<td>5.6 x 10⁶</td>
<td>-36.7</td>
<td>-44.3</td>
</tr>
<tr>
<td>SBR + 10 phr C18amine-MMT</td>
<td>9.5 x 10⁶</td>
<td>-36.7</td>
<td>-43.0</td>
</tr>
<tr>
<td>SBR + 10 phr Na-MMT</td>
<td>3.9 x 10⁶</td>
<td>-38.6</td>
<td>-44.8</td>
</tr>
</tbody>
</table>

Table 3.7. DMTA and DSC data for SBR and SBR/clay nanocomposites with 10 phr clay content.

Figure 3.11a. Relative storage modulus measured with DMTA at 25°C for SBR/clay nanocomposites as a function of volume fraction of silicate.
Figure 3.11b. Relative storage modulus measured with DMTA at 25°C for SBR/clay nanocomposites as a function of volume fraction of organoclay (silicate and surfactant).

Another factor which contributes to the reinforcement of rubber, is the formation of filler network. Filler aggregates in the polymer matrix have a tendency to associate to form agglomerates, especially at high loading, leading to chain-like filler structures or clusters which are termed filler networks [25]. The existence of filler network, especially in carbon black systems, and its impact on rubber properties, with particular emphasis on viscoelastic behavior has been studied in depth over the past 50 years [26]. In the case of carbon black filled systems, the percolation threshold of the filler network separates the modulus enhancement into two regimes [27]. The modulus increase is much stronger above the percolation threshold, when the filler concentration reaches a value where the single particles (or aggregates) become into contact and can form a filler network. Schon
and Gronski [15] recently have indicated that the percolation threshold appears to be about 4.4 vol.% of silicate in organoclay-filled SBR systems at room temperature. This value is less than for silica filled systems (9.5 vol.%) due to the anisotropic characteristic of the clay fillers. For SBR/C18DMB-MMT and SBR/C18amine-MMT, the percolation threshold also tends to be around 4.4 vol.% of silicate (Figure 3.11a) or 9 vol% organoclay (Figure 3.11b). In the case of SBR/VODAC-MMT, the percolation threshold is lower (in between 2.3 and 4.4 vol% of silicate) since the slope of the relative modulus begins to change around 2.3 vol% (Figure 3.11a). Figure 3.12 also illustrates the percolation threshold for VODAC-MMT: at room temperature, the storage modulus increases much more after silicate volume fraction of 2.3% (10 phr).

![Figure 3.12. Storage modulus measured with DMTA for SBR/VODAC-MMT nanocomposites.](image-url)
The tan delta values obtained from DMTA measurements are plotted in Figure 3.13 for 30 phr clay. Tan delta is the ratio of the storage modulus over the loss modulus. From the curves, the intensity of tan delta peak at the glass transition temperature (Tg) decreases with each type of organoclay. The position of the tan delta peak corresponding to the Tg of the nanocomposites does not shift significantly from pure SBR as demonstrated in Table 3.6. These results agree with the Tg obtained by DSC. According to Schon and coworkers [14, 15] the decrease in intensity of the tan delta peak can be used as an indication of higher degree of intercalation/exfoliation. When a greater amount of polymer is in between the clay layers the amount of polymer in the amorphous matrix is reduced. The sample with VODAC-MMT showed greatest decrease in tan delta, and it decreased by more than a half at the 30 phr. These results correlate very strongly with TEM micrographs in terms of nano-scale dispersion of the clay.

Figure 3.13. Tan delta measured with DMTA for SBR and SBR nanocomposites with 30 phr clay.
Another feature observed in the tan delta plots is that the values for organoclays tend to increase at temperatures higher than 20°C. This behavior is related to the filler network relaxation process, shown in Figure 3.14, in which the strain imposed at higher temperatures causes the breakage of filler contacts and sliding of the silicate platelets [14, 15]. The organoclay filler network is made up of anisotropic clay sheets and stacks of platelets linked to each other at single contact points in most cases. As these platelets are flexible in the polymer matrix in comparison to silica aggregates, their linkages are relatively stable at lower temperatures (below 30°C), but after they are broken apart, they will not reform as easily [15].

![Figure 3.14. Schematic of filler network in SBR/clay nanocomposites and effect of strain.](image)

### 3.3.3 Barrier Property

Oxygen flux \( J(t) \) at 0% relative humidity was measured using OXTRAN® 2/20 (MOCON) unit, which employs the continuous-flow cell method approved ASTM (Designation: D3985-81). This method is generally adopted for measurement of oxygen permeation through polymers. Nitrogen was used as the carrier gas and pure oxygen was used as the test gas. Prior to the test, the rubber membrane was conditioned in pure nitrogen inside the unit to remove traces of atmospheric oxygen. Conditioning was especially important to measure non-steady state oxygen flux from which the diffusion coefficient \( D \) was determined. Then, oxygen was introduced to the test cell. The test
ended when the flux reached a steady state. Figure 3.15 shows a schematic of the test cell in MOCON.

Figure 3.15. Schematic of inner chamber of the O\textsubscript{2} test cell in Mocon.

Figure 3.16 shows typical experimental $J(t)$ curves describing the oxygen flux through SBR, SBR/NaMMT, and different SBR/clay nanocomposites. The curve with SBR/VODAC-MMT showed lowest flux in comparison with other samples. All curves consisted of a non-steady state and a steady state region. The non-steady state region, associated with the progress of concentration profile across the thickness, is mainly determined by the diffusion coefficient, $D$. As the permeant concentration in the specimen reached a constant contribution, the flux reached the steady-state value, $J_0$. This value normalized by the membrane thickness $l$ and permeant pressure $p$ defined the permeability $P = J_0lp^{-1}$.

In order to obtain the diffusion coefficient and to accurately determine the permeability coefficient, the data was fit to the solution of Fick’s second law:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

(1)
The boundary conditions for the permeant concentration were \( c(x = 0, t) = S_p \), and \( c(x = l, t) = 0 \), where \( S \) is the solubility coefficient; \( p \), the gas pressure; and \( l \) is the sample thickness. The initial condition was \( c(x, t = 0) = 0 \) and the solution to Eq. (1) is:

\[
J(t) = \frac{P_p}{l} \left[ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-D \pi^2 n^2 t / l^2) \right]
\] (2)

Permeability, \( P \), and diffusion coefficient, \( D \), were obtained by performing a two-parametric least square fit of experimental flux data to Eq. (2), which describes the flux at the end of the membrane \( (x = l) \). The solubility, \( S \), was obtained from the relationship \( P = DS \). The fitting curves are included with the experimental points in Figure 3.16. The fits were equally good for all the experiments in this study. There is a lag period of 10 to 15 minutes for the oxygen to diffuse through the membrane and reach the test sensor.

Figure 3.16. Experimental oxygen flux versus time data and fits to Fick’s law for SBR, SBR/NaMMT and SBR/clay nanocomposites.
The results for oxygen permeability, diffusion coefficient, and solubility of the SBR samples are presented in Table 3.8 and plotted in Figure 3.17. The effects of surfactant chain length, functional group reactivity and clay content on transport properties are observed.

<table>
<thead>
<tr>
<th>Rubber</th>
<th>Permeability</th>
<th>Diffusion coeff.</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cc cm / m² day atm)</td>
<td>Ps/Pp</td>
<td>(m²/s)</td>
</tr>
<tr>
<td>SBR</td>
<td>56.75</td>
<td>1.00</td>
<td>5.18E-11</td>
</tr>
<tr>
<td>5 phr NaMMT</td>
<td>53.29</td>
<td>0.94</td>
<td>4.59E-11</td>
</tr>
<tr>
<td>10 phr NaMMT</td>
<td>50.25</td>
<td>0.89</td>
<td>4.42E-11</td>
</tr>
<tr>
<td>20 phr NaMMT</td>
<td>46.97</td>
<td>0.83</td>
<td>4.20E-11</td>
</tr>
<tr>
<td>30 phr NaMMT</td>
<td>43.37</td>
<td>0.76</td>
<td>4.03E-11</td>
</tr>
<tr>
<td>5 phr VODAC</td>
<td>46.55</td>
<td>0.82</td>
<td>4.59E-11</td>
</tr>
<tr>
<td>10 phr VODAC</td>
<td>38.66</td>
<td>0.68</td>
<td>4.01E-11</td>
</tr>
<tr>
<td>20 phr VODAC</td>
<td>28.11</td>
<td>0.50</td>
<td>3.79E-11</td>
</tr>
<tr>
<td>30 phr VODAC</td>
<td>23.06</td>
<td>0.41</td>
<td>3.28E-11</td>
</tr>
<tr>
<td>5 phr C18DMB</td>
<td>49.16</td>
<td>0.87</td>
<td>4.74E-11</td>
</tr>
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<td>10 phr C18DMB</td>
<td>44.83</td>
<td>0.79</td>
<td>4.20E-11</td>
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<td>0.66</td>
<td>4.06E-11</td>
</tr>
<tr>
<td>30 phr C18DMB</td>
<td>28.76</td>
<td>0.51</td>
<td>3.69E-11</td>
</tr>
<tr>
<td>5 phr C18amine</td>
<td>47.62</td>
<td>0.84</td>
<td>4.56E-11</td>
</tr>
<tr>
<td>10 phr C18amine</td>
<td>43.30</td>
<td>0.76</td>
<td>4.25E-11</td>
</tr>
<tr>
<td>20 phr C18amine</td>
<td>31.68</td>
<td>0.56</td>
<td>3.63E-11</td>
</tr>
<tr>
<td>30 phr C18amine</td>
<td>25.63</td>
<td>0.45</td>
<td>3.34E-11</td>
</tr>
<tr>
<td>5 phr VDAC</td>
<td>49.64</td>
<td>0.87</td>
<td>4.51E-11</td>
</tr>
<tr>
<td>10 phr VDAC</td>
<td>44.63</td>
<td>0.79</td>
<td>4.40E-11</td>
</tr>
<tr>
<td>20 phr VDAC</td>
<td>37.61</td>
<td>0.79</td>
<td>3.77E-11</td>
</tr>
<tr>
<td>30 phr VDAC</td>
<td>36.53</td>
<td>0.64</td>
<td>4.00E-11</td>
</tr>
</tbody>
</table>

Table 3.8. Permeability, diffusion coefficient and solubility for SBR and SBR/clay nanocomposites.
According to the data, SBR with VODAC-MMT demonstrated the highest decrease in permeability: 32% and 60% for 10 and 30 phr of clay, respectively. Samples with C18DMB-MMT showed similar behavior but not as intense: permeability decreased by 21% and 49% for 10 and 30 phr of clay, respectively. In the case of 10 phr VDAC-MMT the decrease in permeability was similar to C18DMB-MMT, but at 30 phr the permeability decreased by only 36%. SBR/C18amine-MMT nanocomposites displayed a decrease in permeability slightly higher than SBR/C18DMB-MMT but not as good as
VODAC-MMT nanocomposites. Finally, for untreated clay, the smallest permeability decreases were observed: 11% and 24% for 10 and 30 phr Na-MMT, respectively. These results are in agreement with the TEM morphology indicating that VODAC-MMT provides better dispersion and higher aspect ratio than any other clay. The reactivity of VODAC-MMT contributes to the clay nano-dispersion and the enhancement in the barrier properties. Similar reasoning can be used for VDAC-MMT in comparison with C18DMB-MMT; even though VDAC has a shorter chain length, it is reactive unlike C18DMB. However, with the shorter chain length of VDAC, the availability of the reactive group is not as great as in VODAC, hence the difference in property.

In the case of oxygen diffusion through the rubber, the presence of highly dispersed clay layers in the SBR/VODAC-MMT nanocomposites increases the tortuosity, which decreases the diffusion. Thus, VODAC-MMT samples have the smallest diffusion coefficient among all samples (Table 3.8). The solubility typically decreases proportionally to the filler content as in the case of SBR/NaMMT, shown in Figure 3.18. At the same time, the solubility decreased the most for VODAC-MMT nanocomposite because of the nano-dispersion. Based on the tan delta values of DMTA and the TEM analysis, SBR/VODAC-MMT showed highest amount of intercalation/exfoliation corresponding to a greater amount of polymer in between the clay layers and a reduced amount of polymer in the amorphous matrix. This reduction of the rubber in the amorphous phase led to the steepest decrease in the solubility.
Figure 3.18. Oxygen solubility data for SBR samples with NaMMT, C18DMB-MMT, C18amine-MMT, VDAC-MMT, and VODAC-MMT.

3.4 CONCLUSIONS

SBR/clay nanocomposites were synthesized via mechanical mixing using a Brabender mixer and a 2-roll mill. Montmorillonite functionalized with four different types of surfactant was used: commercially available C18amine, and laboratory synthesized C18DMB, VDAC, and VODAC. The surfactant chain length and functional groups affected the dispersion of clay nanolayers in the matrix and the overall properties of the nanocomposites. XRD revealed peaks corresponding to intercalated structures for all system; however, with TEM, partial exfoliation was also observed for samples with long chain surfactants. SBR/VODAC-MMT had highest level of exfoliation and highest
aspect ratio in comparison with other nanocomposites. Considerable mechanical and barrier reinforcement was achieved over pure rubber. In particular for SBR/VODAC-MMT, the oxygen permeability decreased the most, by 60%, with the addition of 15 wt.% inorganic filler. Nanocomposites containing functionalized clay with surfactants of shorter chain (VDAC) or different functional groups (C18DMB and C18amine) showed smaller permeability reduction, by 36%, 49%, and 55% respectively. The best performance of nanocomposites containing VODAC-MMT is attributed to the presence of the vinyl-benzyl group and the 18 carbon-atom chain in the surfactant which provides higher compatibility with SBR and greater dispersion of the organoclay, increasing the tortuous path for gas diffusion through the rubber.

3.5 REFERENCES


CHAPTER 4
MODELING OF BARRIER AND MECHANICAL PROPERTIES OF RUBBER/CLAY NANOCOMPOSITES

4.1 INTRODUCTION

Polymer nanocomposites have been intensely researched in the last decade since the addition of a small quantity of reinforcement fillers (up to 10wt.%) such as clays in the polymer matrix have led to improvements of mechanical [1-3] and barrier [5-13] properties. Barrier property improvements, in particular, have made polymer/clay nanocomposites a promising technology for a multitude of packaging applications [14]. The presence of silicate layers in nanocomposites improves the gas barrier properties of the nanocomposites by reducing the polymer volume accessible for gas transport and also by creating a tortuous path for the diffusing species. Yano et al. [8] prepared exfoliated polyimide-clay hybrid in which addition of 2 wt.% (1 vol.%) of montmorillonite reduced permeability of several gases such as oxygen, helium, and water vapor to values less than half of those found for pure polymer. Also, rubber/clay nanocomposites have shown great potential for tire application with increased retention of air pressure. Kojima et al. [13] synthesized a rubber clay hybrid from nitrile rubber and clay (3.9 vol.%) in which the permeability of hydrogen and water vapor were 70% of those in pure acrylonitrile-butadiene rubber (NBR). Studies of gas transport in rubber/clay nanocomposites, however, are fairly recent. At the same time, considerable enhancement in mechanical properties of various types of polymer/clay nanocomposites (including rubber systems) have been achieved through optimization of molecular interactions between reinforcing agents and matrix and through reduction in size of the reinforcing fillers [15]. Kim et al.
[3] reported NBR/clay nanocomposites with a storage modulus 10 times higher than pure rubber at 0°C when 12 wt.% of organoclay ion exchanged with octadecylamine was used.

Even though a few papers have reported permeability and modulus of nanocomposites in the literature, most of these do not correlate theoretical predictions with experimental data due to the early theoretical stage on property enhancements in nanocomposites. Several factors such as silicate dispersion and orientation must be taken into account to achieve reasonable predictions for the behavior of nanocomposites. Gas barrier in polymer clay nanocomposites was traditionally explained in terms of Nielsen model, originally adopted to describe the tortuosity effect of plate-like particulates on gas permeability of polymer filled composite structures. Nielsen model [16] predicts the effect of filler composition on gas permeability in the model system consisting of uniform platelets homogeneously dispersed in the polymer matrix and oriented parallel to the polymer film surface. When this structural assumption is met, the model typically shows a good agreement with experimental data as in the case of polymer films or thin sheets with plate-like particulates (talc, mica, metal flakes) added to increase gas barrier [17]. Parallel platelet orientation presumably gives a better gas barrier performance as compared to random platelet orientation. Recently, Bharadwaj [18] modified the Nielsen model to predict gas barrier in the case of randomly dispersed silicates. However, the correlations between aspect ratios predicted form these models and the actual morphology of the nanocomposites need further research since the models over estimate the actual aspect ratio of the fillers. The same can be said for modulus prediction, since only Shia et al.[15] have attempted to correlate the theory and experiments in
poly(dimethyl siloxane) (PDMS)/clay nanocomposite. Most of the theories for predicting mechanical properties were developed for reinforced conventional composites.

In this chapter, different gas transport models (Nielsen, Bharadwaj, Cussler, and Fredrickson) are applied to describe the behavior of oxygen through rubber/clay nanocomposites. Also, three types of modulus models are used to predict the behavior of these nanocomposites. The actual morphology of the nanocomposites observed by transmission electron microscopy (TEM) and x-ray diffraction (XRD) from the previous chapter is used to determine the quality of these models and to possibly improve their prediction.

4.2 OXYGEN TRANSPORT

4.2.1 Nielsen Model

Nielsen model [16] predicts the effect of filler composition on gas permeability in the model system consisting of uniform platelets homogeneously dispersed in the polymer matrix and oriented parallel to the polymer film surface. The model can be applied, using equation 1, to obtain the clay aspect ratio from the permeability data of these nanocomposites. In the equation, \( P \) is the permeability of the nanocomposite, \( P_0 \) is the permeability of the pure polymer, and \( \phi_f \) is the volume fraction of the clay. \( L \) and \( W \) are length and width of the clay sheets, respectively; its ratio, \( L/W \), defines the aspect ratio, \( \alpha \), of the fillers. The model assumes that the fillers are impermeable to the diffusing gas or liquid molecule, and are oriented perpendicular to the diffusion direction. Thus, the presence of the filler particles creates a tortuous path for the permeant to travel through the composites. The denominator on the right hand-side of equation (1) is also referred to
the tortuosity factor, \( \tau \), defined as the distance a molecule must travel to get through the film \( (d') \) divided by the thickness of the film \( (d) \). Figure 4.1 illustrates Nielsen’s approach.

\[
\frac{P}{P_0} = \frac{1 - \phi_f}{1 + \frac{L}{2W} \phi_f}
\]

(1)

Figure 4.1. Path of the diffusing gas molecule through polymer containing clay platelets in Nielsen model.

The permeability data measured for SBR/clay nanocomposites are plotted in Figure 4.2 and fit with Nielsen model. The curves show a good fit of the data, and clearly, as the clay content increases, the permeability decreases. The aspect ratios calculated are compared with the ones calculated from TEM in Table 4.1. The samples with greater dispersion such as the partially exfoliated SBR/VODAC-MMT presented the highest aspect ratio. With lower dispersion and more aggregates such as in SBR/VDAC-MMT, the aspect ratio decreased by more than a half. Another observation is that the aspect ratios from Nielsen model are roughly twice as large as the TEM values. The difficulty in determining the aspect ratios from TEM is that the pictures could not be taken a higher magnification. Thus the accuracy, specially, for determining the thickness of the clay nanolayers is not very high and the error indicated can be large.
From Table 4.1, the aspect ratios determined from TEM do not change significantly with clay content for SBR/VODAC-MMT; it appears that at 20 phr the aspect ratio increases slightly as also observed from the permeability data (point is a little lower than curve with $\alpha = 40$). For C18DMB-MMT, the aspect ratio decreased from 12 to 8 as the clay content doubled from 5 to 10 phr. In the case of C18amine-MMT, the aspect ratio increased from 13 to 19 with clay content changed from 10 to 20 phr, which was also observed from the permeability data. For VDAC-MMT, the aspect ratio decreased from 11 for 5 phr to 5 and 4 for 10 and 20 phr clay, respectively. These differences in aspect ratio indicate that the type of surfactant used significantly affects the clay dispersion. Furthermore, as observed by TEM micrographs from Chapter 3, the aspect ratio for each type of nanocomposites at different clay loading are fairly similar and Nielsen model can fit the data very well.
Figure 4.2. Permeability data for SBR/NaMMT, and SBR/clay nanocomposites fit with Nielsen model.

Table 4.1. Aspect ratios calculated for SBR/clay nanocomposites from TEM and from Nielsen model.

<table>
<thead>
<tr>
<th></th>
<th>Aspect Ratio From TEM</th>
<th>Aspect Ratio From Nielsen</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR 5 phr</td>
<td>20 ± 7</td>
<td>40</td>
</tr>
<tr>
<td>SBR 10 phr</td>
<td>19 ± 11</td>
<td></td>
</tr>
<tr>
<td>SBR 20 phr</td>
<td>23 ± 8</td>
<td></td>
</tr>
<tr>
<td>VODAC-MMT</td>
<td>12 ± 8</td>
<td>22</td>
</tr>
<tr>
<td>C18amine-MMT</td>
<td>13 ± 11</td>
<td>26</td>
</tr>
<tr>
<td>VDAC-MMT</td>
<td>5 ± 4</td>
<td>18</td>
</tr>
</tbody>
</table>

4.2.2 Bharadwaj Model

Recently, Bharadwaj [18] modified Nielsen model to incorporate an orientation parameter $S$, in which a range of relative orientations of the clay sheets with respect to
each other represented by \( \theta \) (the angle between the direction of preferred orientation and the sheet normal) could be applied. Bharadwaj’s expression is shown in equation (2) accompanied by orientation parameter equation (3):

\[
\frac{P}{P_0} = \frac{1 - \phi_f}{1 + \frac{L}{2W} \phi_f \left( \frac{2}{3} \right) \left( S + \frac{1}{2} \right)} \quad (2)
\]

\[
S = \frac{1}{2} \left( 3 \cos^2 \theta - 1 \right) \quad (3)
\]

In the case of random platelet orientation \( (S = 0) \), the tortuosity decreases with orientation and diffusion is facilitated as opposed to parallel orientation \( (S = 1 \text{ or Nielsen model}) \). The model predicts higher aspect ratios for the nanocomposites in order to fit the data precisely as shown in Figure 4.3. The aspect ratios are more than double the ones from Nielsen model. From the TEM micrographs, the observed aspect ratios are much smaller than from Bharadwaj model. Also, the majority of the clay layers appear to be oriented in the same direction (parallel to the membrane surface and perpendicular to the gas flow), rather than randomly oriented. Therefore, this model is not applicable to describe gas transport thorough rubber/clay nanocomposites discussed in this thesis.
4.2.3 Cussler Model

Another model used to describe gas behavior though a membrane was developed by Cussler et al. [19-22] with focus on the diffusion of a small gas molecule through a matrix partly filled with impermeable flakes. The flakes are oriented perpendicular to the direction of diffusion (similar to Nielsen model), and have one very long dimension so that the diffusion is essentially two-dimensional. The diffusion is mainly related to three factors: the tortuous wiggles to get around the flakes, the tight slits between the flakes, and the resistance of going from the wiggle to the slit. The model (equation 4) assumes
that the diffusion depends on the aspect ratio and volume fraction of the impermeable filler:

\[
\frac{D}{D_0} = \frac{1}{1 + \frac{(L/2W)^2 \phi_f^2}{(1 - \phi_f)}} \quad (4)
\]

Where \( D \) is the diffusion coefficient of the composites, \( D_0 \) is the diffusion coefficient of the pure polymer.

A permeability model can be obtained by multiplying the diffusion (equation 4) by the appropriate solubility. Since the model assumes linear relationship between solubility of filled composites and volume fraction, \( S = S_0(1-\phi) \), where \( S \) is the solubility of the filled composites and \( S_0 \) is the solubility of pure polymer. The permeability expression is the following:

\[
\frac{P}{P_0} = \frac{(1-\phi_f)^2}{1 - \phi_f + (L/2W)^2 \phi_f^2} \quad (5)
\]

Figure 4.4 illustrates the Cussler model curves fitting the permeability data of two rubber/clay nanocomposites (SBR/VODAC-MMT and SBR/C18DMB-MMT). The curves do not fit the data well. In fact, it appears that at higher concentrations the aspect ratio decreases; that is more than one curve is needed to describe the behavior of a particular sample. For SBR/VODAC-MMT up to 10 phr, the aspect ratio calculated is 60 or higher; at 20 phr and 30 phr, the aspect ratio is around 40. However, the TEM demonstrates that the dispersion is very homogeneous up to 30 phr of clay content. Cussler model, then, cannot be applicable for rubber/clay nanocomposites.
Figure 4.4. Permeability data for SBR/clay nanocomposites fit with Cussler model.

4.2.4 Fredrickson model

Fredrickson model [23] uses a systematic approach to transport properties of dilute particle dispersions based on multiple scattering expansion and disk-shaped particles as basis. It models two distinct regimes: dilute and semidilute. The dilute regime resembles Nielsen model and accounts for low filler content. Fredrickson modified Nielsen by adding a geometric factor, $K = \pi/\ln \alpha$, into the equation:

$$\frac{D}{D_0} = \frac{1}{1 + K \alpha \phi_f}$$

where $\alpha = L/2W$
Fredrickson expresses Nielsen model with diffusion coefficient, $D$, instead of permeability since the volume fraction of filler applied is small (less than 0.1) and thus the solubility can be assumed constant (remember $P = DS$). For the semidilute regime, the filler content has increased from the dilute regime, and the system resembles Cussler model, which Fredrickson modified so that the aspect ratio is higher than Cussler’s. He indicated that Cussler model calculates a lower aspect ratio than expected. In the modified Cussler model, the aspect ratios is higher, and a geometric factor, $\mu$, was added:

$$\frac{D}{D_0} = \frac{1}{1 + \mu \alpha^2 \phi_f^2}$$

where $\mu = \pi^2/(16 \ln^2 \alpha)$

The term, $1-\phi_f$, from the original Nielsen and Cussler models were approximated to the value of 1 for the modified versions.

Fredrickson also derived a function $F_2(K\alpha\phi_f)$ to be used for the transition between dilute and semidilute regimes; i.e. it connects Nielsen and Cussler models:

$$F_2(x) = \left( \frac{1}{1 + a_1 x} + \frac{1}{1 + a_2 x} \right)^2$$

where $a_1 = (2-\sqrt{2})/4$ and $a_2 = (2+\sqrt{2})/4$, and $x = K\alpha\phi_f$

The parameter, $x = K\alpha\phi_f$, is used to distinguishes the dilute from semidilute regimes. The modified Nielsen model works in a regime where the factor $K\alpha\phi_f$ is smaller than 3, Fredrickson function, $F_2(K\alpha\phi_f)$, can be used for $3 \leq K\alpha\phi_f \leq 12$, and the modified Cussler model is appropriate for $K\alpha\phi_f > 12$. Figure 4.5 shows the curves modified by Fredrickson. The modified Cussler model gives a much higher aspect ratio than the original Cussler model but the fit is still inadequate. Fredrickson function $F_2(K\alpha\phi_f)$ appears very similar to Nielsen model, and gives the same aspect ratio as the modified
Nielsen ($\alpha = 50$) in an attempt to fit the SBR/VODAC-MMT data. The original Nielsen and the modified Nielsen models are very similar to each other, except that the aspect ratio is slightly higher for the modified model. For the rubber/clay nanocomposites discussed in this dissertation, the parameter $K\alpha \phi_f$ is below 3 for all samples, including the highest concentration of 30 phr. This indicates that the nanocomposites are in the dilute regime, and thus, Nielsen model should be used to fit the data. Also, the original Nielsen model gives the closest value of aspect ratio as observed with TEM.

Figure 4.5. Permeability data for SBR/clay nanocomposites fit with Fredrickson model.
4.3 MODULUS

The improvement in modulus for polymer/clay nanocomposites are much higher than for conventional composites at similar clay content. Since the majority of theoretical predictions were developed for composite systems, in the case of nanocomposites these predictions are not very applicable. Shia et al. [15, 24] applied a model for composites developed with aligned platelet inclusions to PDMS/clay nanocomposites. The experimental modulus indicated that the rate of modulus increase decreased with increasing volume fraction (up to 0.04) of filler. The model predictions did not agree well with the experiments. The justification for this was based on imperfect bonding between the matrix/inclusion interface which effectively reduces the aspect ratio and volume fraction of the inclusion. Instead, the model assumed perfect bonding, and the modulus is predicted to increase with filler content. However, because of the lack of publication on modulus predictions of nanocomposites, it is difficult to verify if imperfect bonding is a phenomenon that can be applied in general to all nanocomposites.

The storage modulus of the SBR/clay nanocomposites described in chapter 3 are very opposite to the results by Shia et al. [15]; here, the modulus rate increases with filler content. An attempt to fit the modulus of SBR/VODAC-MMT at room temperature with three different models is illustrated in Figure 4.6. The models applied are based on Halpin-Tsai [25], Modified Rule of Mixtures (MROM) [26], and Hui and Shia [24]. In all of them, the aspect ratio, \( \alpha \), specified is 100 (in the case of Halpin-Tsai and Hui and Shia \( \alpha \) is expressed as \( 1/100 \)). None of these models are very accurate but MROM is the closest to predicting the appropriate trend.
The Halpin-Tsai equation often used for fiber-reinforced composites has been modified for flakes [25] and is described below:

\[
\frac{E}{E_0} = \frac{1 + \omega B \phi_f}{1 - \Psi B \phi_f} \tag{6a}
\]

where

\[
B = \frac{(E_1 / E_0) - 1}{(E_1 / E_0) + \omega}, \quad \omega = 1.33 \alpha^{0.645} \tag{6b}
\]

and

\[
\Psi = 1 + \frac{1 - \phi_m^3}{\phi_m^3} \phi_f \tag{6c}
\]

E, E₀, and E₁ refer to the actual modulus, the modulus of the matrix (without filler), and the modulus of the filler, respectively. E₁ has been estimated as the value for mica, \(1.7 \times 10^{11}\) Pa [27]. \(\phi_m\) is the maximum packing fraction of the platelets and varies between 0.785 and 0.907. However, this variation produced only minor changes in the predictions of the modulus and the value of 0.907 was used.

The Hui and Shia equations used are the following:

\[
\frac{E}{E_0} = \frac{1}{1 - \frac{\phi_f}{4} \left[ \frac{1}{\xi} + \frac{3}{\xi + \Lambda} \right]} \tag{7a}
\]

\[
\xi = \phi_f + \frac{E_0}{E_1 - E_0} + 3(1 - \phi_f) \left[ \frac{(1 - g) \alpha^2 - (g/2)}{\alpha^2 - 1} \right] \tag{7b}
\]

\[
\Lambda = \left(1 - \phi_f\right) \left(\frac{3g(\alpha^2 + 0.25) - 2\alpha^2}{\alpha^2 - 1}\right) \tag{7c}
\]

\[
g = \pi/2 \alpha \tag{7d}
\]
and the MROM equations used were:

\[
E = \phi_f E_f (MRF) + E_0(1 - \phi_f) \tag{8a}
\]

\[
(MRF) = \left(1 - \frac{\tanh(u)}{u}\right), \quad u = \alpha \sqrt[2]{\frac{\phi_f G_0}{E_i(1 - \phi_f)}} \tag{8b}
\]

where \( G_0 \) is the shear storage modulus of the matrix defined as:

\[
G_0 = \frac{E_0}{2(1 + P)} \tag{8c}
\]

where \( P \) is the Poisson’s ratio is 0.25 [26]. In equation 8b, MRF is the “modulus reduction factor” which is a fraction \( \leq 1 \), approaching unity with increasing flake aspect ratio, reinforcement volume fraction, and matrix shear stiffness.

Figure 4.6. Relative modulus of SBR/VODAC-MMT nanocomposite compared with prediction from models for conventional reinforced composites.
These model predictions underestimate the modulus as a function of clay content. Besides, the aspect ratio of 100 is much higher (5x) than observed experimentally from TEM in Table 4.1. The MROM prediction was derived semi-empirically to fit samples with $E_1/E_0$ between 25 (flake/aluminum matrix) and 500 (flake/plastic resin). In the SBR/clay nanocomposites $E_1/E_0$ is on the order of $10^4$, which exceeds the limit for MROM, but the trend of the prediction agrees the best with experimental behavior. In fact, if $\alpha$ is assumed to be 125, then the model fits perfectly the data. The Hui Shia and Halpin Tsai models can fit the relative modulus at very low values of volume fraction (0.01-0.023), but break down at higher $\phi_f$ (still low filler content).

4.4 CONCLUSIONS

The oxygen transport through rubber/clay nanocomposites was predicted by four theoretical models (Nielsen, Bharadwaj, Cussler, and Fredrickson). Nielsen prediction gave the best data fit indicating that the aspect ratio of each type of nanocomposite is for the most part similar at different clay concentrations. The differences in oxygen permeability and aspect ratios are significant for rubber nanocomposites with clay ion exchanged by different surfactants. Fredrickson model suggested that the nanocomposite data was in the dilute regime, and thus, Nielsen model should be used for the fit. The other two models were not appropriate: Bharadwaj excessively over predicted the aspect ratios of the silicates, and Cussler model could not fit the data with one curve and the same aspect ratio. Further research is needed in this field since the aspect ratio calculated from Nielsen model is not the same (double) as observed experimentally via TEM. The modulus prediction demonstrated similar results with the gas transport models; MROM
resulted in the best fit for the modulus of SBR/VODAC-MMT with the exception that the aspect ratio calculated was 125 versus 20 observed by TEM. These models developed for conventional composites do not account for the nano-dispersion of the layered silicates.

4.5 REFERENCES


CHAPTER 5

EFFECTS OF CARBON BLACK ON SBR
AND SBR/CLAY NANOCOMPOSITES

5.1 INTRODUCTION

Carbon black is the most important reinforcing filler used in the rubber industry. About 90% of the worldwide production of carbon black is used in the tire industry in which the carbon black improves tear strength, modulus, and wear characteristics of the tires [1]. Carbon black consists essentially of elemental carbon in the form of nearly spherical particles of colloidal size, coalesced into particle aggregates and agglomerates, which are obtained by the partial combustion or thermal decomposition of hydrocarbons. The carbon black aggregates are built from primary particles tightly fused together so that the particles cannot be separated by normal processing techniques used for rubber. A group of aggregates together forms an agglomerate, but the aggregate is the smallest dispersible unit of carbon black, not the primary particle. The unique ability of carbon black to enhance the physical properties of elastomers is associated with the size, shape, and surface chemistry of the primary aggregates [2].

Since the origin of carbon black is from petroleum, it causes pollution and gives the rubber a black color. In the past two decades, research was aimed to develop other reinforcing agents to replace carbon black in rubber compounds such as sepiolite, kaolin, and precipitated silica [3]. These fillers are inorganic in nature and incompatible with organic polymer matrices. Thus, the reinforcing effect was much lower than with carbon black. However, with the development of nanocomposites, it is possible to tailor the surface of the silicate layers to become organophilic which can enhance the properties of
the polymer significantly. Indeed, some rubber/clay nanocomposites reported in the literature have mechanical properties similar to or better than rubber filled with carbon black [3-6]. Arroyo et al. [3] prepared natural rubber nanocomposites with 10 phr organoclay with similar modulus, tensile strength and hardness as natural rubber with 40 phr carbon black. Magaraphan et al. [4] also prepared natural rubber nanocomposites with 7 phr of MMT functionalized with octadecylamine which presented higher tensile strength and elongation than NR with 20 phr carbon black. The effect of carbon black on rubber/clay nanocomposites has never been reported in the literature.

In this chapter, SBR filled with carbon black was synthesized and compared with SBR/clay nanocomposites. At the same time, the synergistic behavior of organoclay and carbon black was investigated in SBR samples, which contained both fillers at different concentrations. The improvements in mechanical and barrier properties were analyzed. The combination of two different fillers can lead to different types of filler networks which will be discussed here.

5.2 EXPERIMENTAL

5.2.1 Materials

The elastomer used for preparing nanocomposites was SBR (Nipol 1502; Mooney viscosity according to ML (1+4) at 100°C = 52; styrene content 23 wt.%) supplied by the Zeon Corporation. MMT used in this study was provided by Southern Clay Products (under the trade name of Mineral Colloid BP) and contains exchangeable cations of primarily Na⁺. Mineral Colloid BP is a fine powder with an average particle size of 75µm in the dry state, and a cation exchange capacity (CEC) of 90mEq/100g. The
following surfactants used to ion exchange the clay were synthesized in the laboratory as described in chapter two: vinylbenzyl octadecylimethyl ammonium chloride (VODAC) [7], and octadecyldimethyl betaine (C18DMB). [8]. Carbon black (CB) supplied by Cabot Corporation was grade Vulcan M (or N339), which has a small particle size (about 29 nm), high surface area (approximately 90 m$^2$/g), and is a reinforcing type carbon black. The ingredients used in processing the rubber included zinc oxide, stearic acid, and sulfur supplied by Harwick Standard, agerite stalite and copper dimethyldithiocarbamate (cummate) by R.T. Vanderbilt, and benzoathiazyl disulfide (MBTS) by AkroChem. Zinc oxide and stearic acid react with the accelerator enabling it to exert its full function. Agerite stalite is used as an antioxidant. Sulfur is used exclusively for vulcanization. MBTS is the accelerator most extensively used today for vulcanization of SBR and cummate is an ultra-accelerator used at small quantity with MBTS.

5.2.2 Processing

SBR nanocomposites containing clay and/or carbon black were prepared by mixing the rubber, zinc oxide (5 phr), stearic acid (2 phr), agerite stalite (1 phr), clay and/or carbon black in a Brabender mixer (Plasti-Corder PL 2000) for 10 minutes at 80°C. The compound was then milled in a 2-roll mill (Farrel) at room temperature with the vulcanizing agents: sulfur (2 phr), MBTS (1.5 phr), and cummate (0.1 phr). The vulcanization was achieved by compression molding at 160°C for 20 minutes. The samples prepared are listed in Table 5.1, which also gives the weight and volume fraction of the fillers carbon black (CB) and modified MMT. The densities of the carbon black and MMT were 1.8 g/cm$^3$ and 2.6 g/cm$^3$. 
<table>
<thead>
<tr>
<th></th>
<th>CB</th>
<th>CB / VODAC-MMT</th>
<th>CB / C18DMB-MMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>phr</td>
<td>10</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>CB wt. fract.</td>
<td>0.082</td>
<td>0.152</td>
<td>0.264</td>
</tr>
<tr>
<td>CB vol. fract.</td>
<td>0.047</td>
<td>0.090</td>
<td>0.165</td>
</tr>
<tr>
<td>MMT wt. fract.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MMT vol. fract.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total filler wt. fract.</td>
<td>0.095</td>
<td>0.130</td>
<td>0.191</td>
</tr>
<tr>
<td>Total filler vol. fract.</td>
<td>0.046</td>
<td>0.067</td>
<td>0.107</td>
</tr>
</tbody>
</table>

Table 5.1. Samples prepared for SBR nanocomposites containing carbon black (CB) and/or organoclays (VODAC-MMT or C18DMB-MMT) and their respective weight and volume fraction.

5.2.3 Characterization

X-ray diffraction (XRD) measurements were made using a Rigaku RINT 2000 wide angle x-ray diffractometer (40kV, 40 mA) equipped with a Ni-filtered Cu-Kα (1.5418 A) source. Transmission Electron Microscopy (JEOL 1200 EX TEM) operated at 80 kV was used to investigate the nano-structure of SBR/clay nanocomposites. The ultrathin sections with a thickness of 100 nm were microtomed at -80°C using a MT-7000 ultramicrotome. The direction of the compression mold relative to the TEM samples surface was perpendicular. Oxygen flux, J(t), at 25ºC, 0% relative humidity and 1 atm pressure were measured with a OX-TRAN® 2/20 (MOCON) unit, which employs a continuous-flow cell method approved by ASTM (Designation: D 3985-81). Tensile strength and strain tests were carried out according to ISO 37 using a Shimazu Autograph ABS-1000 at crosshead speed of 50 cm/min. The average of three tests is reported here. The hardness was measured according to ISO 48 using a type A Durometer. The tensile strength, strain, and hardness measurements were provided by Yokohama Rubber Company (YRC). Dynamic mechanical properties were measured using a Dynamic...
Mechanical Thermal Analyzer (DMTA) from Rheometric Scientific. The samples (0.5 x 10 x 25 mm³) were swept at 3°C min⁻¹ from -90°C to 80°C at a frequency of 1 Hz. The storage modulus (E’), the loss modulus (E”’) and mechanical loss factor (tan δ) were determined.

5.3 RESULTS AND DISCUSSION

5.3.1 Mechanical Properties

Fillers such as carbon black when added to polymer matrices are known to cause considerable change in dynamic properties of the composites [9]. Stress-strain properties for SBR samples filled with carbon black and/or organoclay are presented in Table 5.2. Tensile strength at break at 10 phr carbon black (12.7 MPa) is similar to the SBR/VODAC-MMT nanocomposite at the same filler content. At 40 phr of carbon black, however, it almost tripled as shown in Figure 5.1. One of the reasons for such improvement is the reduction of the inter-aggregate distance within the fillers which imposes greater resistance against crack propagation [1]. The modulus at 200%, 300%, and 400% elongation increased significantly with carbon black content as compared to unfilled SBR. Elongation at break increased and then decreased as the carbon black content increased from 10 to 40 phr (Figure 5.2). At high loading, the compound becomes stiffer, since the volume fraction of the rubber in the composite decreases [10]. The high hardness with 40 phr carbon black demonstrates the stiffness of the composite (Figure 5.3). When VODAC-MMT was mixed together with carbon black each at 10 phr, the mechanical improvement (tensile strength and hardness) was similar as to SBR with 40 phr carbon black (Figures 5.1 and 5.3). The presence of the clay improves the
elongation more than with the isotropic filler (Figure 5.2). The longer clay particles provide more interfacial contact for the rubber molecules allowing for greater extensions. The property improvements were better when VODAC-MMT was used instead of C18DMB-MMT in combination with carbon black. The styrenic functional group of VODAC renders a more compatible organoclay with SBR than C18DMB, and the silicate dispersion with VODAC was greater than with C18DMB as observed from Chapter 3. The results from Table 5.2 indicate that it is possible to achieve almost the same mechanical enhancement with half the amount of filler when combining VODAC-MMT with carbon black (10 phr each) versus carbon black only at 40 phr.

<table>
<thead>
<tr>
<th>Rubber</th>
<th>Modulus 100% (MPa)</th>
<th>Modulus 200% (MPa)</th>
<th>Modulus 300% (MPa)</th>
<th>Modulus 400% (MPa)</th>
<th>Tensile Strength at break (MPa)</th>
<th>Elongation at break (%)</th>
<th>Hardness (JIS-A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>0.9</td>
<td>1.3</td>
<td>1.8</td>
<td>--</td>
<td>4.0</td>
<td>227</td>
<td>46</td>
</tr>
<tr>
<td>10 phr CB</td>
<td>1.2</td>
<td>2.2</td>
<td>4.1</td>
<td>7.3</td>
<td>12.7</td>
<td>507</td>
<td>52.7</td>
</tr>
<tr>
<td>10 phr VODAC-MMT</td>
<td>1.8</td>
<td>2.6</td>
<td>3.4</td>
<td>4.5</td>
<td>12.3</td>
<td>602</td>
<td>60</td>
</tr>
<tr>
<td>10 phr C18DMB-MMT</td>
<td>1.4</td>
<td>2.0</td>
<td>2.6</td>
<td>3.3</td>
<td>7.9</td>
<td>583</td>
<td>57</td>
</tr>
<tr>
<td>40 phr CB</td>
<td>4.0</td>
<td>11.6</td>
<td>20.9</td>
<td>27.3</td>
<td>31.9</td>
<td>427</td>
<td>68.1</td>
</tr>
<tr>
<td>10 phr CB + 10 phr VODAC-MMT</td>
<td>2.3</td>
<td>4.2</td>
<td>6.9</td>
<td>11.0</td>
<td>30.6</td>
<td>614</td>
<td>61.7</td>
</tr>
<tr>
<td>10 phr CB + 10 phr C18DMB-MMT</td>
<td>2.1</td>
<td>3.7</td>
<td>6.2</td>
<td>10.4</td>
<td>26.8</td>
<td>583</td>
<td>59.3</td>
</tr>
</tbody>
</table>

Table 5.2. Mechanical properties of SBR filled with carbon black and/or organoclays.
Figure 5.1. Tensile strength at break of SBR with carbon black and/or organoclays.

Figure 5.2. Elongation at break of SBR with carbon black and/or organoclays.
Figure 5.3. Hardness of SBR with carbon black and/or organoclays.

The addition of carbon black to SBR also improves appreciably the storage modulus of pure SBR depending on the amount of filler added as shown in Figure 5.4. For a small amount of carbon black, such as 10 phr (8.2 wt.%) the increase in room temperature (25°C) modulus is only 30%; however, at 40 phr (26.4 wt.%) the modulus increases by more than 3 times that of plain SBR. With increasing the carbon black content, the aggregates tend to associate into agglomerates or clusters which are generally termed secondary structure or filler network. The formation of the filler network is responsible for such an improvement in modulus as the content of carbon black increases. Since carbon black is a filler with high affinity toward hydrocarbon rubber, the filler network can be formed primarily by a joint shell mechanism. The polymer chains adsorb on the filler surface which reduces the mobility of the polymer segment. This results in a
rubber shell with a high modulus near the surface of the filler but as the polymer chains distance themselves from the surface, the modulus gradually decreases and finally reaches the same level as that of the polymer matrix [11]. When two or more aggregates are close enough, they form an agglomerate via a joint rubber shell where the modulus of the occluded polymer is higher than that of the polymer matrix. The immobilized polymer chains attached to the filler, lead to an increase in effective volume fraction of the filler causing enhancement in dynamic properties such as elastic modulus [9]. According to Wang [12], for a rubber vulcanizate filled with 50 phr carbon black, having volume fraction of 0.197 based on filler density, the measured relative modulus at 70°C, (0.8% strain and 10 Hz) was equivalent to that of a vulcanizate having a filler volume fraction of 0.462 obtained from the Van der Poel theory [13]. Moreover, Payne, who studied the elastic modulus as a function of strain amplitude for carbon black filled rubber, observed that at low strain, the modulus increased exponentially with increasing filler concentration [14]. Figure 5.5 shows the relative storage (\(E_{\text{composite}}/E_{\text{SBR}}\)) modulus as a function of volume fraction of carbon black at various temperatures. In the rubbery state (temperatures above -20°C below), the modulus begins to increase exponentially with increasing volume fraction of carbon black from 0.09 to 0.17 for curves at 25°C and 70°C. At -40°C, SBR is in the transition state and the modulus is much lower than in the composites which are still in the glassy state due to their higher glass transition temperature as observed by the shifts in tan delta peaks in Figure 5.7 discussed later. At –70°C (glassy state), the rubber is very viscous with a very high storage modulus, and the addition of a hard filler such as carbon black resulted in much smaller modulus enhancement than in the rubbery state.
Figure 5.4. Storage modulus measured with DMTA for SBR and SBR filled with carbon black.

Figure 5.5. Relative modulus for SBR/carbon clack composites at different temperatures.
When organoclays are mixed with carbon black, the effect on the storage modulus is superior compared to only carbon black. In Figure 5.6, for sample with 10 phr CB and 10 phr VODAC-MMT, the storage modulus, 16 MPa at 25°C, is the same as observed with 40 phr CB, which contains twice as much filler. With 20 phr carbon black and 10 phr VODAC-MMT, the modulus increases even more over the entire temperature range (i.e. 23 MPa at 25°C). When C18DMB-MMT is used instead of VODAC-MMT, the improvement in storage modulus is not as great (11 MPa at 25°C). This was also observed for the tensile properties, demonstrating that VODAC-MMT brings best reinforcement.

![Figure 5.6. Storage modulus measured with DMTA for SBR and SBR filled with mixtures of carbon black and organoclay.](image)

As mentioned in chapter 3 the tan delta can be used as an indicator to the dynamic hysteresis of the rubber. When the polymer is below Tg, in the glassy state, the energy dissipation is low since the viscosity of the polymer is very high and the chains can
hardly move. With increasing temperature the movement of the polymer segments increase; at Tg, the molecular adjustments are easier, the storage modulus decreases and the energy dissipation among the polymer molecules increases resulting in a high hysteresis. At temperatures above the Tg (rubbery state), the molecular adjustment is quick enough to follow the dynamic strain and the hysteresis is low. Figures 5.7 and 5.8 shows the tan delta curves of SBR/carbon black composites and SBR filled with a mixture of carbon black and organoclay, respectively. In the case of carbon black filler only (Figure 5.7), the formation of filler network is responsible for the decrease in hysteresis at low temperatures (around Tg or below) when compared to the pure rubber since the unbound rubber fraction is reduced [9]. As the temperature increases, the decrease in tan delta is attenuated since the thickness of the trapped rubber shell around the filler decreases and the rubber chains eventually become part of the rubber matrix, which contributes to energy dissipation.

![Diagram](image)

Figure 5.7. Tan delta measured with DMTA for SBR and SBR/carbon black composites.
The tan delta behavior in a system with just organoclay is somewhat similar to silica filled rubbers as observed in Chapter 3, but different from carbon black filled systems. In SBR/clay nanocomposites part of the rubber is intercalated within the clay layers and a decrease in the intensity of the tan delta peak is observed. Also, the filler network consists of highly anisotropic platelets and stacks of platelets linked to each other at single contact points. Since the platelets are flexible, their linkages are stable at temperatures above Tg but below room temperature (25°C) [15]. As the temperature increases above 25°C, the filler network begins to break down and reform; untrapped rubber volume fraction increases and internal friction among the silicates contribute to energy dissipation as observed by the increase in the tan delta curve.
In the SBR systems containing a mixture of carbon black and organoclay (Figure 5.8), characteristics of both carbon black and organoclay are observed: the decrease in tan delta peak (around -30°C) with increasing overall filler content, and an increase in tan delta as temperature increases (around 60°C). An attempt to explain this behavior in greater detail will be done by using the mixed system of carbon black and silica studied by Wang [9] and shown in Figure 5.9 extracted from reference [9]. Even though silica and carbon black are spherical particles, silica is very different than carbon black: highly polar and incompatible with hydrocarbon rubber [16]. In rubber, as the silica content increases, the filler network forms primarily by direct contact between aggregates and it is very rigid. But above a certain strain level or temperature (40°C from Figure 5.9) the network can be rapidly destroyed. The carbon black filler network, formed primarily by joint shell mechanism, is less rigid and begins to break down at a lower strain or temperature (30°C from Figure 5.9) than the silica; however, the break down of the carbon black network proceeds less rapidly [9]. When both fillers are used simultaneously, three different types of filler networks are observed: a silica filler network, a carbon black filler network, and a weak silica-carbon black filler network. The reason for a weak carbon black-silica filler network can be concluded from Figure 5.9 in which the system with 50/50 loading shows the highest hysteresis at temperatures higher than 30°C. The weak silica-carbon black interaction in this case is easily broken down and reformed at temperatures of 30°C or higher, leading to a greater hysteresis than those of compounds filled with the individual filler.
Figure 5.9  Temperature dependence of tan delta for vulcanizates filled with carbon black (N234) / silica (HiSil 210) blends [9].

A similar plot is presented for constant loading of clay/carbon black shown in Figure 5.10. For the system with an equal loading of carbon black and organoclay, the curve presents characteristics of both fillers: the high hysteresis characteristic of the carbon black system at temperatures above T_g but below 30°C, and the high hysteresis characteristic of the organoclay system at temperatures higher than 40°C. The tan delta curve falls in between the pure carbon black and organoclay systems. Therefore, three types of filler network can be expected similarly to the silica-carbon black system: carbon black filler network, organoclay filler network and organoclay-carbon black filler network. The organoclay-carbon black network is most likely stronger than for the case of silica-carbon black network since the breakdown and reformation of the network begins at a higher temperature (40°C) than the organoclay system (20°C), and the hysteresis is in between the carbon black and VODAC-MMT systems.
5.3.2 Barrier Property

The effect of carbon black on the permeability of a rubbery compound is not as significant as the improvement in mechanical properties. Van Amerongen reported a 30% decrease in oxygen permeability for natural rubber filled with 22% by volume of carbon black [17]. That is a relatively high volume fraction of filler for a small decrease in permeability. Other fillers such as clay bentonite (untreated) will reduce the permeability by 70% at that concentration as reported in the literature [17] and in Chapter 3.

Oxygen permeability, diffusion coefficient and solubility have been measured and calculated for SBR samples with carbon black at 10, 20, and 40 phr along with samples containing a mixture of clay and carbon black: 5, 10, and 20 phr CB, 10 phr VODAC-
MMT, and 10 phr CB with 10 phr C18DMB-MMT. The results are shown in Figure 5.11 and Table 5.3. Due to spherical nature of carbon black filler, the decrease in permeability is not very significant as expected, even with a high filler loading (40 phr or 26.4 wt.% CB).

![Figure 5.11. Permeability for SBR and SBR nanocomposites with carbon black and/or organoclays.](image)

The permeability, however, is reduced considerably when carbon black is mixed with organoclay. In the case of SBR/VODAC-MMT/CB both at 10 phr, permeability decreased by almost 30%. Similar result was observed if C18DMB-MMT was used. It is possible to obtain significant decrease in permeability of SBR rubber with a mixture of 10 phr clay and 10 phr carbon black, which totals to a filler content of only 6.7% by volume (Figure 5.11). Such combinations can be a valuable tool for the industry since the
total amount of filler is about half of a sample of SBR with 40 phr carbon black, and the permeability decreases by almost 10% more.

From Figure 5.11, it can be observed, furthermore, that a small content of carbon black (10 phr or less) does not affect the permeability significantly (within experimental error); permeability of SBR with 10 phr carbon black is similar to SBR, and the permeabilities of SBR/clay nanocomposites (10 phr of VODAC-MMT or C18DMB-MMT) filled with carbon black (10 phr or less) are not much different from the nanocomposites without carbon black. Nevertheless, doubling the carbon black content in SBR to 20 phr will intensify the drop in the permeability but not as much as the doubling the organoclay content described in Chapter 3. This reduction in permeability is associated in part with the solubility and diffusion of the oxygen gas in the samples. Carbon black is a very adsorbent material and this well know capacity for adsorbing gas is retained after it is incorporated into rubber [18]. Amerongen [18] concluded that the gas adsorbed on carbon black does not contribute to the actual permeation process, thus the diffusion coefficient is reduced for carbon black filled rubbers. The decrease in the diffusion coefficient and the increase in solubility due to the carbon black can be seen in the results of Table 5.3. Also, the formation of filler network may contribute to the decrease in permeability. As mentioned before, with the build up of the filler network, the rubber becomes trapped within the filler agglomerates leading to an increase in the effective filler volume fraction. The trapped rubber has a higher glass transition temperature than the amorphous rubber [9], thus the lower mobility of these molecules will slow down the gas diffusion.
<table>
<thead>
<tr>
<th>Rubber</th>
<th>Permeability (cc cm / m³ day atm)</th>
<th>Diffusion coeff. (m²/s)</th>
<th>Solubility (cc / cm³ atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>56.75</td>
<td>5.18E-11</td>
<td>0.128</td>
</tr>
<tr>
<td>SBR + 10 phr CB</td>
<td>54.96</td>
<td>3.75E-11</td>
<td>0.170</td>
</tr>
<tr>
<td>SBR + 20 phr CB</td>
<td>46.64</td>
<td>3.13E-11</td>
<td>0.173</td>
</tr>
<tr>
<td>SBR + 40 phr CB</td>
<td>43.97</td>
<td>2.35E-11</td>
<td>0.220</td>
</tr>
<tr>
<td>SBR + 5 phr CB + 10 phr VODAC-MMT</td>
<td>41.41</td>
<td>3.58E-11</td>
<td>0.136</td>
</tr>
<tr>
<td>SBR + 10 phr CB + 10 phr VODAC-MMT</td>
<td>40.19</td>
<td>3.18E-11</td>
<td>0.147</td>
</tr>
<tr>
<td>SBR + 10 phr CB + 10 phr C18DMB-MMT</td>
<td>41.02</td>
<td>3.35E-11</td>
<td>0.142</td>
</tr>
<tr>
<td>SBR + 20 phr CB + 10 phr VODAC-MMT</td>
<td>32.91</td>
<td>2.60E-11</td>
<td>0.147</td>
</tr>
</tbody>
</table>

Table 5.3. Permeability, diffusion coefficient, and solubility for SBR samples prepared with carbon black and/or VODAC-MMT or C18DMB-MMT.

5.3.3 Morphology

X-ray diffraction plots of the SBR/carbon black and SBR/clay nanocomposites filled with carbon black are illustrated in Figure 5.12. The rubber with carbon black alone does not have any prominent peak in the 2-10 degree range as expected since the filler particles are spherical aggregates. In the case of SBR/clay nanocomposites with carbon black, three main peaks are observed, indicating mainly rubber intercalation (d = 3.33 nm for C18DMB-MMT and 3.15 nm for VODAC-MMT) and also few collapsed layers (d = 1.70 and 1.23 nm for both nanocomposites). These peaks are similar to the XRD of SBR/clay nanocomposites without carbon black, including the peaks for the collapsed layers.
Figure 5.12. XRD of SBR, SBR containing 10 phr carbon black, and SBR/clay nanocomposites (10 phr VODAC-MMT or C18DMB-MMT) filled with 10 phr carbon black.

TEM micrographs of SBR with carbon black and SBR/VODAC-MMT nanocomposite filled with carbon black are shown in Figure 5.13. The non-uniform carbon black agglomerates are easily detected, and as demonstrated in the permeability results, they offer little tortuosity. In the case of nanocomposite with carbon black, the clay layers appear intercalated with some partial exfoliation, and the calculated average aspect ratio of 19 is in agreement with the nanocomposite without carbon black discussed in Chapter 3.
Figure 5.13. TEM micrographs of (a) SBR filled with 10 phr carbon black (mag-15 K), and (b) SBR/VODAC-MMT containing carbon black with 10 phr each filler (mag-25 K).

5.4 CONCLUSIONS

SBR/clay nanocomposites filled with carbon black were synthesized and compared with the SBR compounds with carbon black only. While carbon black alone (40 phr) offered great improvement in the mechanical properties of the rubber, the synergism of organoclay and carbon black brought similar property enhancements with only half the total filler loading (10 phr each filler). Also, SBR nanocomposites containing a mixture of two fillers showed improved barrier property in comparison with compound having only carbon black. The morphology appeared to be intercalated with some partial exfoliation of the silicate layers as observed by TEM. These results indicate that nanocomposites containing a mixture of organoclay and carbon black can be a substitute for rubber filled with carbon black only. The clay-carbon black nanocomposites offer similar, if not better, performance in tires or other potential applications.
5.5 REFERENCES


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CHAPTER 6

SYNTHESIS AND CHARACTERIZATION OF OTHER RUBBER-CLAY
NANOCOMPOSITE SYSTEMS: NR AND Br-IIR

6.1 INTRODUCTION

Rubber/clay nanocomposite technology has been extended to other systems besides styrene-butadiene rubber. In terms of rubber/clay nanocomposites with improved barrier properties, only systems with acrylonitrile-butadiene rubber (NBR) and ethylene propylene diene methylene (EPDM) have been studied. NBR/clay nanocomposites with 4% clay by volume has 30% lower permeability than pure rubber for hydrogen and water vapor [1]. EPDM/clay nanocomposites showed similar 30% decrease in permeability with 4 wt. % organoclay [2]. Other rubbery systems such as silicone rubber, epoxidized natural rubber and natural rubber have demonstrated mechanical property enhancements but no gas transport behavior has been reported.

In the case for natural rubber (NR), Arroyo et al. [3] developed nanocomposites containing 10 phr MMT treated with octadecylamine with enhanced mechanical properties such as a 350% increase in tensile strength (15 MPa) and higher hardness (43.5 shore A) in comparison with NR (4.25 MPa and 29 shore A, respectively). This reinforcement in properties with 10 phr organoclay was comparable with 40 phr carbon black. Varghese and Karger-Kocsis [4] used NR latex and mixed with organoclay forming NR nanocomposites of high stiffness and low damping characteristics. The same authors [5] also developed NR nanocomposites via melt compounding with 10 phr of commercial organoclays or pristine layered silicates (fluorohectorite or bentonite). The nanocomposites containing 10 phr organoclay (Nanomer I.30P) presented high
mechanical property improvements: storage modulus (3750 MPa at -70°C), tensile strength (19 MPa) and hardness (42 shore A). Joly et al. [6] prepared intercalated NR/clay nanocomposites with some exfoliated silicates which also indicated (qualitatively) superior modulus than the pure rubber. Finally, Magaraphan et al. [7] synthesized NR/clay nanocomposites via solution technique, indicating exfoliation of clay layers by x-ray diffraction and transmission electron microscopy. Samples with 7 phr organoclay presented similar tensile strength (32 MPa) as NR filled with 20 phr carbon black and higher than unfilled NR (19 MPa).

In this chapter, NR/clay and bromo-butyl rubber (Br-IIR)/clay nanocomposites were developed. The main focus was on oxygen gas transport through the nanocomposites. Different types of organoclays were used and compared to pure rubber. In the case of Br-IIR, some mechanical properties were also determined. The morphologies of the nanocomposites were analyzed to help understand the enhancement of properties.

6.2. EXPERIMENTAL

6.2.1 Materials

The elastomers used for preparing nanocomposites were natural rubber (NR) RSS#3 from Mitthai Nakorn Co. and bromobutyl rubber (Br-IIR), grade 2244, (Mooney viscosity according to ML (1+8) at 125°C = 46) supplied by ExxonChemical. Mooney viscosity is a widely used notation to characterize rubber; it is recorded with a rotational viscometer with a large rotor if the term “ML” is indicated. The terms “1” and “8” represent the preheat time (minutes) before the rotor starts to turn, and the time of actual rotation of the rotor before the final Mooney viscosity measurement is made, respectively.
Br-IIR consists of brominated isobutylene (98%) / isoprene (2%) copolymers; hence, the abbreviation Br-IIR. MMT used in this study was provided by Southern Clay Products (under the trade name of Mineral Colloid BP) and contains exchangeable cations of primarily Na⁺. Mineral Colloid BP is a fine powder with an average particle size of 75 µm in the dry state, and a cation exchange capacity (CEC) of 90mEq/100g. The following surfactants used to ion exchange the clay were synthesized in the laboratory as described in chapter two: vinylbenzyl octadecyldimethyl ammonium chloride (VODAC) [8] and octadecyldimethyl betaine (C18DMB) [9]. Octadecylamine was purchased from Aldrich. The ingredients used during the rubber processing such as zinc oxide, stearic acid, and sulfur were supplied by Harwick Standard, agerite stalite and tetramethylthiuramdisulfide (TMTD) by R.T. Vanderbilt, and benzoathiazyl disulfide (MBTS) by AkroChem. Zinc oxide and stearic acid react with the accelerator enabling it to exert its full function. Agerite stalite is used as an antioxidant. Sulfur is used exclusively for vulcanization. MBTS and TMTD are common accelerators used for vulcanization of rubber.

6.2.2 Processing

NR-clay nanocomposites were prepared by mixing the rubber, zinc oxide (5 phr), stearic acid (2 phr), agerite stalite (1 phr), and clay in a Brabender mixer (Plasti-Corder PL 2000) for 6 minutes at 80°C. The compound was then milled in a 2-roll mill (Farrel) at room temperature with the vulcanizing agents: sulfur (2.75 phr), MBTS (1 phr), and TMTD (0.1 phr). Br-IIR nanocomposites were prepared by mixing the rubber, stearic acid (1 phr), and clay in a Brabender mixer (Plasti-Corder PL 2000) for 6 minutes at
80°C. The compound was then milled in a 2-roll mill (Farrel) at room temperature with zinc oxide (3 phr) and the vulcanizing agents: sulfur (1.7 phr), MBTS (1 phr), and TMTD (1.25 phr). The vulcanization was achieved by compression molding NR and Br-IIR at 160°C for 10 and 25 minutes, respectively. The samples prepared are listed in Table 6.1, which also gives the weight and volume fractions of the inorganic filler. The organoclays contain roughly 15 to 30 wt.% of surfactant (depending on the molecular weight of each surfactant), but the volume and weight fraction in Table 6.1 accounts for only the silicate content in order to compare the nanocomposites with similar inorganic material.

<table>
<thead>
<tr>
<th>Clay type</th>
<th>NR 5 phr</th>
<th>NR 10 phr</th>
<th>NR 7.5 phr</th>
<th>Br-IIR 5 phr</th>
<th>Br-IIR 10 phr</th>
<th>Br-IIR 7.5 phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>VODAC-MMT (wt. fract.)</td>
<td>0.030</td>
<td>0.058</td>
<td>0.046</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VODAC-MMT (vol. fract.)</td>
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<td>0.022</td>
<td>0.018</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C18DMB-MMT (wt. fract.)</td>
<td>0.032</td>
<td>0.062</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C18DMB-MMT (vol. fract.)</td>
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<td>0.024</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C18amine-MMT (wt. fract.)</td>
<td>0.034</td>
<td>0.066</td>
<td>0.052</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C18amine-MMT (vol. fract.)</td>
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<td>0.025</td>
<td>0.020</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-MMT (wt. fract.)</td>
<td>0.043</td>
<td>0.082</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-MMT (vol. fract.)</td>
<td>0.016</td>
<td>0.032</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Table 6.1. Types of clays used for NR and Br-IIR nanocomposites and their respective silicate weight and volume fraction

6.2.3 Characterization

X-ray diffraction (XRD) measurements were made using a Rigaku RINT 2000 wide angle x-ray diffractometer (40 kV, 40 mA) equipped with a Ni-filtered Cu-Kα (1.5418 A) source. Transmission Electron Microscopy (JEOL 1200 EX TEM) operated at 80 kV was used to investigate the nano-structure of NR/clay nanocomposites. The
ultrathin sections with a thickness of 100 nm were microtomed at -100°C using a MT-7000 ultramicrotome. The direction of the compression mold relative to the TEM samples surface was perpendicular. Oxygen flux, \( J(t) \), at 25°C, 0% relative humidity and 1 atm pressure were measured with a OX-TRAN® 2/20 (MOCON) unit, which employs a continuous-flow cell method approved by ASTM (Designation: D 3985-81). For Br-IIR samples the mechanical properties were also measured. Tensile strength and strain tests were carried out according to ISO 37 using a Shimazu Autograph ABS-1000 at crosshead speed of 50 cm/min. The average of three tests is reported here. The hardness was measured according to ISO 48 using a type A Durometer. The tensile strength, strain, and hardness measurements were provided by Yokohama Rubber Company (YRC). Dynamic mechanical properties were measured using a Dynamic Mechanical Thermal Analyzer (DMTA) from Rheometric Scientific. The samples (0.5 x 10 x 25 mm\(^3\)) were swept at 3°C min\(^{-1}\) from -90°C to 80°C at a frequency of 1 Hz. The storage modulus (\( E' \)), the loss modulus (\( E'' \)) and mechanical loss factor (tan δ) were determined.

### 6.3. RESULTS AND DISCUSSION

#### 6.3.1. Natural rubber/clay nanocomposites

The morphology of all NR/clay nanocomposites according to XRD in Figure 6.1 is intercalated. NR/C18DMB-MMT sample showed the highest d-spacing of 3.6 nm corresponding to rubber intercalation, a second peak at 2.1 nm similar to the C18DMB-MMT peak (chapter 2), a third peak at 1.4 nm which indicates a collapse of the layered structure as in the case with SBR (Chapter 3), and a small fourth peak at 1.02 nm (secondary reflection, \( d_{002} \), of the second peak). Collapsed layers, with d-spacing between 1.3 and 1.7 nm, were also observed in NR/clay nanocomposites synthesized by Varghese.
and Karger-Kocsis [5]. One of their nanocomposites contained MMT ion exchanged with octadecylamine which is one of the surfactants used in this work. The proposed explanation for the collapse of the layers (d-spacing is lower than the C18DMB-MMT d-spacing of 2.24 nm) is due to interactions of the surfactant with vulcanizing agents which lead to the surfactant removal from the silicate interlayers causing a decrease in the d-spacing. In accelerated sulfur curing process, zinc present is prone to coordination complexing in which amine groups present in the surfactant and sulfur of the sulfuric curatives may participate [5,10]. NR/C18amine-MMT indicates intercalation with a peak at 3.5 nm and another peak with slightly higher intensity at 1.3 nm corresponding to the collapsed layers. For NR/VODAC-MMT, the peak of 3.00 nm is clearly observed while a very weak peak around 6.5 degrees represents the collapsed silicates. The curve for NR containing Na-MMT illustrates a broad peak around 6.9°, indicating that the d-spacing of the clay increased from 1.04 to only 1.28 nm due to poor rubber intercalation.

TEM micrographs of NR/clay nanocomposites are shown in Figure 6.2; all three systems indicate good nano-dispersion with intercalated layers. In the case of NR/C18amine-MMT, the micrograph reveals thicker aggregates and more randomly dispersed layers than NR/C18DMB-MMT and NR/VODAC-MMT, which have silicate aggregates aligned to each other. The dimensions of the silicate layers are presented in Table 6.2. NR/C18DMB-MMT shows a slightly higher aspect ratio (19) than NR/VODAC-MMT and NR/C18amine-MMT (17).
Figure 6.1. XRD of NR and NR nanocomposites containing 10 phr of VODAC-, C18amine-, C18DMB-, and Na-MMT
Figure 6.2. TEM micrographs of (a) NR/C18DMB-MMT, (b) NR/C18amine-MMT, and (c) NR/VODAC-MMT at 10 phr organo-clay content.

<table>
<thead>
<tr>
<th>NR + 10 phr</th>
<th>C18amine-MMT</th>
<th>VODAC-MMT</th>
<th>C18DMB-MMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (nm)</td>
<td>306</td>
<td>91</td>
<td>320</td>
</tr>
<tr>
<td>Width (nm)</td>
<td>20</td>
<td>7</td>
<td>20</td>
</tr>
<tr>
<td>Aspect Ratio</td>
<td>17</td>
<td>4</td>
<td>17</td>
</tr>
</tbody>
</table>

Table 6.2. Estimated length, width, and aspect ratio of clay sheet for NR/clay nanocomposites.

Gas transport through natural rubber is high in comparison to butyl rubbers or even SBR. The oxygen permeability of NR/clay nanocomposites as a function of the clay content is plotted in Figure 6.3 and listed in Table 6.3. Unlike the SBR systems, NR nanocomposites containing C18DMB-MMT demonstrated better performance than VODAC-MMT and C18amine-MMT. The intercalated system with highest d-spacing presented highest tortuosity leading to the lowest permeability (44.4 cm$^4$/m$^2$ day atm at 10 phr C18DMB-MMT). The aspect ratio of C18DMB-MMT calculated using Nielsen model ranged between 30 and 40 for 5 and 10 phr, respectively. For NR/VODAC-MMT, the smaller d-spacing reduced the effect of tortuosity and the aspect ratio calculated was around 30. In the case of C18amine-MMT, two types of structures, intercalated and
collapsed, are present at similar ratios since the intensity of their particular XRD peaks is very similar (Figure 6.1). TEM (Figure 6.2.b) also showed agglomerates of clay particles corresponding to collapsed layers and random dispersion of the silicates. Thus, the tortuosity is much lower and the permeability is higher than NR/VODAC-MMT, which has similar aspect ratio determined from TEM (Table 6.2) but the layers are aligned with each other giving higher tortuosity to gas flow. For the case of conventional composite, NR/Na-MMT, the barrier reinforcement due to filler is the weakest overall, since the dispersion is very poor; all the layers have d-spacing of 1.3 nm. Nielsen model estimated an aspect ratio of 10. The diffusion coefficient and solubility decreased with clay content similarly to SBR/clay nanocomposites. These gas transport results for NR/clay nanocomposites are completely unique to the literature.

<table>
<thead>
<tr>
<th>Rubber</th>
<th>Permeability (cc cm / m² day atm)</th>
<th>Ps/Pp</th>
<th>Diffusion coeff. m²/s</th>
<th>Solubility (cc / cm³ atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>70.00</td>
<td>1.00</td>
<td>3.66E-11</td>
<td>0.24</td>
</tr>
<tr>
<td>5 phr VODAC</td>
<td>60.10</td>
<td>0.86</td>
<td>3.30E-11</td>
<td>0.21</td>
</tr>
<tr>
<td>10 phr VODAC</td>
<td>50.24</td>
<td>0.72</td>
<td>3.23E-11</td>
<td>0.18</td>
</tr>
<tr>
<td>5 phr C18DMB</td>
<td>60.38</td>
<td>0.86</td>
<td>3.79E-11</td>
<td>0.18</td>
</tr>
<tr>
<td>10 phr C18DMB</td>
<td>44.40</td>
<td>0.63</td>
<td>3.47E-11</td>
<td>0.15</td>
</tr>
<tr>
<td>5 phr C18amine</td>
<td>65.97</td>
<td>0.94</td>
<td>3.65E-11</td>
<td>0.23</td>
</tr>
<tr>
<td>10 phr C18amine</td>
<td>53.57</td>
<td>0.77</td>
<td>3.58E-11</td>
<td>0.18</td>
</tr>
<tr>
<td>10 phr NaMMT</td>
<td>57.10</td>
<td>0.82</td>
<td>3.49E-11</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Table 6.3. Permeability, diffusion coefficient and solubility of NR and its nanocomposites.
Figure 6.3. Permeability data for NR/NaMMT and NR/clay nanocomposites fit with Nielsen model.

6.3.2 Bromo-butyl rubber/clay nanocomposites

XRD shown in Figure 6.4 reveals exfoliated and intercalated morphologies for Br-IIR/clay nanocomposites containing 7.5 phr C18amine-MMT and VODAC-MMT, respectively. The intercalated nanocomposite had d-spacings of 3.45, 2.05 and 1.35 nm, in which the first one corresponds to intercalated rubber, and the others to collapsed clay layers, similar to NR nanocomposites. No peaks were observed for nanocomposite with C18amine-MMT which could indicate that the layers are exfoliated. XRD alone is not sufficient to determine exfoliation; another technique such as TEM is needed to visualize
Due to the very low $T_g$ (approximately –100°C) of the rubber, the high TEM voltage deformed the samples and no pictures could be taken.

Butyl type rubbers have very high barrier towards gas transport. In fact, the polyisobutylene portion of the butyl rubber molecule provides a low degree of permeability to gases and this property leads to an almost exclusive use in inner tubes [12]. Halogenated rubbers such as Br-IIR have low permeability and also ability to adhere to highly unsaturated rubbers, which is why more than 80% of Br-IIR produced is used in tire innerliners. The oxygen permeability for Br-IIR measured was indeed very

Figure 6.4. XRD of Br-IIR and Br-IIR nanocomposites containing 7.5 phr of VODAC-MMT and C18amine-MMT
low in comparison to the other rubbers: 13 and 16 times lower than SBR and NR, respectively. These numbers are in agreement with literature reports. With addition of 7.5 phr of functionalized clay, the permeability was reduced by about 25% for nanocomposite with VODAC-MMT and 23% with C18amime-MMT. These results are shown in Table 6.4 and Figure 6.5. The permeability was not much affected by the type of surfactant used to modify the clay unlike in SBR nanocomposites, even though the morphology of the Br-IIR/clay nanocomposites is different. The slightly higher permeability when C18amime-MMT is used can be related to the results obtained for polystyrene (PS)/clay nanocomposites [13]. The exfoliated PS/clay nanocomposites had higher permeability than intercalated nanocomposites since the exfoliated layers could be grouped in domains of low aspect ratio as shown in Figure 6.6a and the intercalated structure presented a staircase alignment (Figure 6.6b). In the case of Br-IIR/C18amime-MMT, the layers may be grouped into domains as in Figure 6.6a and the tortuosity may not be as high as initially anticipated for exfoliated structure. The tortuosity of Br-IIR/C18amime-MMT must be similar to that of Br-IIR/VODAC-MMT or slightly lower, since the aspect ratios calculated from Nielsen model were 27 and 35, respectively. The diffusion coefficients of both nanocomposites are approximately an order of magnitude lower than for SBR. The solubility, as well, is the lowest in comparison with NR and SBR. With the presence of the silicate layers both the diffusion coefficient and solubility are reduced.
Table 6.4. Permeability, diffusion coefficient and solubility of Br-IIR and its nanocomposites.

<table>
<thead>
<tr>
<th>Rubber</th>
<th>Permeability (cc cm / m² day atm)</th>
<th>Diffusion coeff. P/P (m²/s)</th>
<th>Solubility (cc / cm³ atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromo-butyl rubber</td>
<td>4.39</td>
<td>1.00</td>
<td>5.3E-12</td>
</tr>
<tr>
<td>Br-IIR + 7.5 phr VODAC-MMT</td>
<td>3.31</td>
<td>0.75</td>
<td>4.3E-12</td>
</tr>
<tr>
<td>Br-IIR + 7.5 phr C18amine-MMT</td>
<td>3.40</td>
<td>0.77</td>
<td>4.2E-12</td>
</tr>
</tbody>
</table>

Figure 6.5. Permeability data and fit with Nielsen Model for Br-IIR nanocomposites.
Besides improvement of the barrier property, the Br-IIR/clay nanocomposites demonstrated significant mechanical reinforcement as listed in Table 6.5. Br-IIR/VODAC-MMT showed higher increase in modulus and hardness, but nanocomposite with C18amine-MMT had tremendous enhancement in the tensile strength at break shown in Figure 6.7: almost 6 times higher than the pure rubber. The elongation at break was also much higher for nanocomposite with C18amine-MMT than with VODAC-MMT. These results suggest that the nano-scale dispersion controls the tensile strength of the material; the stress applied in the exfoliated nanocomposite can be distributed to each individual layer and the layers may align themselves for maximum elongation. This was proposed by Boyce et al. [14] who attempted to theoretically explain the increase in tensile modulus of polymer/clay nanocomposites. For Br-IIR/VODAC-MMT, the intercalated layers offer less surface area (polymer coverage) and expose the matrix to more straining than the exfoliated structure; thus, lower tensile strength at break.
Table 6.5. Mechanical properties of Br-IIR/clay nanocomposites.

<table>
<thead>
<tr>
<th>Rubber</th>
<th>Modulus 100% (MPa)</th>
<th>Modulus 200% (MPa)</th>
<th>Modulus 300% (MPa)</th>
<th>Modulus 400% (MPa)</th>
<th>Tensile Strength at break (MPa)</th>
<th>Elongation at break (%)</th>
<th>Hardness (JIS-A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-IIR</td>
<td>0.5</td>
<td>0.8</td>
<td>1.3</td>
<td>2.0</td>
<td>3.0</td>
<td>497</td>
<td>33.7</td>
</tr>
<tr>
<td>7.5 ph VODAC</td>
<td>1.2</td>
<td>2.3</td>
<td>3.4</td>
<td>4.4</td>
<td>6.4</td>
<td>517</td>
<td>45.7</td>
</tr>
<tr>
<td>7.5 phr C18amine</td>
<td>1.0</td>
<td>1.6</td>
<td>2.2</td>
<td>2.9</td>
<td>17.6</td>
<td>709</td>
<td>42.5</td>
</tr>
</tbody>
</table>

Figure 6.7. Tensile strength at break for Br-IIR/clay nanocomposites.

The storage modulus of the nanocomposites was measured with a DMTA from -100°C to 80°C, shown in Figure 6.8. Br-IIR/VODAC-MMT indicated a modulus more than 2 times higher than pure rubber and also slightly higher than C18amine-MMT nanocomposite. These results are similar to the modulus from stress-strain. The tan delta of the nanocomposites had a similar peak to the pure rubber, which is comparable to the results obtained with SBR. These overall results, including mechanical and barrier
properties for Br-IIR/clay nanocomposites, are new to the literature, and no other data on these systems have been reported.

Figure 6.8. Storage modulus measured with a DMTA for Br-IIR/clay nanocomposites and Br-IIR.

6.4. CONCLUSIONS

Natural rubber/clay and bromo-butyl rubber/clay nanocomposites were synthesized. Three different types of organoclays were used with natural rubber, and their nanocomposites were intercalated. NR/C18DMB-MMT had lowest permeability and the clay layers were aligned with each other giving high tortuosity to gas diffusion. NR/C18amine-MMT was well dispersed as viewed by TEM. However, the clay layers were randomly located reducing the tortuosity of the filler and giving a higher
permeability than the other two NR nanocomposites. Br-IIR/C18amine-MMT showed no peaks and apparently exfoliated structure via x-ray diffraction, and was almost 3 times stronger than intercalated Br-IIR/VODAC-MMT. Both nanocomposites had similar oxygen permeability: 25% lower than pure rubber for 7.5 phr organoclay content. In the case of the Br-IIR/C18amine, the clay layers may be randomly dispersed but grouped into domains of similar tortuosity as the intercalated structure; hence, similar gas diffusion.

6.5. REFERENCES


CHAPTER 7
SYNTHESIS OF POLYMER GEL ELECTROLYTE WITH HIGH MOLECULAR WEIGHT POLY(METHYL METHACRYLATE)-CLAY NANOCOMPOSITE

7.1 INTRODUCTION

Research on polymer electrolytes has been growing since 1973 when Fenton et al. [1] developed complexes of alkali metal ions with poly(ethylene oxide) (PEO). PEO has been the most popular polymer researched so far, since Armand et al. [2, 3] demonstrated that it could be used as a battery electrolyte. Unfortunately, PEO solid electrolytes give conductivities that are too low for most applications, especially at low temperature. Below 50°C, PEO electrolytes form a crystalline phase that is much less conductive than the preferred amorphous phase. The search for enhanced ionic conductivity has led to the addition of inorganic fillers to polymer electrolytes, in particular for PEO matrixes [4-13]. While still a very active area of research, it appears that dispersed ceramic powders of nanoscale particle size influence the recrystallization kinetics of the PEO polymer chains, thus promoting localized amorphous regions and enhancement of ionic conductivity at room temperature [8].

Although not widely studied as ceramic powders, montmorillonite (MMT) clay is another type of inorganic filler that enhances the conductivity of PEO [14-17] and poly(acrylonitrile) (PAN) [18]. This conductivity increase is due to the well-dispersed clay in the system, which tends to disrupt the association of lithium cations and anions [16]. In the case of the PEO/LiClO₄/clay system, at low clay concentration, such as 2.9%, the clay sheets are exfoliated and act as a Lewis base because the negative charges in the clay surface can complex with the lithium cations. Consequently, the clay can reduce the
interaction between the polymer ether groups and the lithium cations and also the interaction between lithium cations and anions. The presence of clay, only 2.9% with respect to PEO, increased the number of free ions that act as charge carriers, enhancing the ionic conductivity up to 45 times the original PEO/LiClO₄ system without clay. Similar behavior was observed in the case of PAN/LiCF₃SO₂/clay system, in which the clay influences the interactions between the salt cation and anion, causing an increase in the conductivity by almost two orders of magnitude with 6% clay [18]. Recently, Chen et al. [19] also have developed a dry, plasticized PMMA/LiClO₄(25)/EC(75) polymer nanocomposite electrolyte containing 5% clay with ionic conductivity of 6.0x10⁻⁴ S/cm, almost 40 times higher than that without clay. The nanocomposite was synthesized via polymerization in toluene with the resulting PMMA having a low molecular weight, 15,000-20,000, and the clay was ion-exchanged with dimethyldioctadecyl ammonium chloride. Also, Jacob et al. [20] have synthesized a nanogel electrolyte based on poly(vinylidene fluoride)-hexafluoropropylene copolymer (PVDF-HFP) with 5 wt.% of silicate, giving 4.4 x 10⁻⁴ S cm⁻¹ conductivity at room temperature.

The need for improvement in ionic conductivity of polymer electrolyte has also led to the development of polymer gel electrolytes [21]. Generally a polymeric gel is defined as a system consisting of a polymer network swollen with solvent [22]. Due to the presence of the solvent, the overall ionic conductivity reflects the conductivity of the liquid electrolyte solvent(s) rather than of the solid polymer electrolyte [23]. The use of poly(methyl methacrylate) (PMMA) as the polymer matrix for gel electrolyte has been studied extensively in the last decade [24-37], and the major focus is on its application for a secondary lithium battery. One advantage of PMMA gel electrolyte in comparison with
PAN gel electrolyte is that it is less reactive to the lithium electrode [28]. PEO has good stability to lithium but is unstable to high voltage cathodes used in many Li-ion cells.

In this Chapter, we utilize the properties of PMMA/MMT nanocomposite to synthesize a novel polymer nanocomposite gel electrolyte. The MMT is initially dispersed in the monomer (MMA) that is then polymerized forming a high molecular weight PMMA-clay nanocomposite, in which the clay is intercalated or partially exfoliated [38,39]. The polymer nanocomposite is dissolved in a solvent mixture – ethylene carbonate (EC) and propylene carbonate (PC) – along with lithium perchlorate (LiClO$_4$) as salt. The ionic conductivity is compared for gels with different clay concentrations. The dispersion of clay in the nanocomposite gels was characterized by x-ray diffraction (XRD) as well as by transmission and scanning electron microscopy (TEM and SEM, respectively). FTIR was used to explore the interactions of polymer and clay with the solvent and lithium salt.

7.2 EXPERIMENTAL

7.2.1 Materials

MMT used in this study was provided by Southern Clay Products (under the trade name of Mineral Colloid BP) and contains exchangeable cations of primarily Na$^+$. Mineral Colloid BP is a fine powder with an average particle size of 75 µm in the dry state, and a cation exchange capacity (CEC) of 90 mEq/100g. MMA was purchased from Aldrich Chemical and purified by distillation under reduced pressure at 35°C. The free radical initiator, 2,2-azobis (isobutyronitrile) (AIBN), was obtained from DuPont and purified by re-crystalization twice in methanol. The zwitterionic surfactant, octadecyl dimethyl betaine (C18DMB), was synthesized in the laboratory [40]. Electrolyte grade
ethylene carbonate (EC) and propylene carbonate (PC) electrolyte grade, were supplied by Ferro Corporation. Lithium perchlorate, LiClO$_4$, supplied by GFS Chemicals, was vacuum dried at 120°C for 24 hours.

### 7.2.2 Ion exchange of clay and PMMA-clay nanocomposites

Montmorillonite is originally hydrophilic, and must be converted to hydrophobic or organophilic clay in order to be compatible with the polymer matrix. Meneghetti and Qutubuddin [38] have reported ion exchange of the Na$^+$ in MMT with C18DMB. An aqueous solution of 12 mmoles of C18DMB, which also contained 1 mL of HCL (0.027 mole), was added with continued stirring to a clay-water dispersion. The mixture was stirred for 6 hours and left idle overnight. The product was then filtered, washed several times with hot distilled water until no chloride was detected with 0.1 M AgNO$_3$ solution, and vacuum dried. The cation exchanged MMT was ground using a mortar and pestle, and particles with size less than 65 µm were collected. Thermogravimetric analysis indicated that the organophilic clay contained approximately 30 wt.% of surfactant. The ion-exchanged clay was dispersed in the monomer and upon heating and addition of AIBN initiator, polymerization took place. PMMA-clay nanocomposites were synthesized in which clay concentration was varied from 0 to 10 wt.%. A clay concentration of 5 wt.% gave partially exfoliated nanocomposite, while 10 wt.% clay formed an intercalated nanocomposite [38]. To determine the molecular weight, the polymer was extracted from the polymer/clay nanocomposite by swelling in tetrahydrofuran (THF), filtered and then analyzed using gel permeation chromatography (GPC). Molecular weight for the pure PMMA was 334,000, while that for the PMMA 10% clay nanocomposite was 548,000 [39].
7.2.3 Polymer nanocomposite gel electrolyte

The gel composition used for the electrolyte is given below:

PMMA-clay nanocomposite: 30 / PC: 19 / EC: 46.5 / LiClO$_4$: 4.5 by weight.

The PMMA-clay nanocomposite contained a clay concentration of 1, 3, 5, or 10 wt.%, which corresponds to a maximum of 3 wt.% of the total gel electrolyte. The ratio of polymer to solvent to salt was the same as that used by Appetecchi et al. [26]. PMMA-clay nanocomposite and pure PMMA were dried in vacuum at 70°C for 16 hours before used in the electrolyte synthesis. All the components were transferred to a dry Vacuum Atmosphere Company (VAC) glove box with a nitrogen atmosphere, where the gels were made. The moisture content in the dry box was less than 1 ppm. The PMMA-clay nanocomposite was added to the EC/PC solution containing LiClO$_4$. The mixture was heated to 40°C for 2 hours, then to 70°C for 1 hour, and finally compressed between two glass sheets at room temperature to form a 350 µm thick film.

7.2.4 Characterization

Ionic conductivity measurements (performed in the nitrogen glove box) were done by placing the gel electrolyte film between two stainless steel blocking electrodes in a cell apparatus. The films had a thickness of 0.35 mm, determined by a Teflon spacer, and an area of 1.44 cm$^2$. A Solartron (model 1280 B) was used to supply an alternating current frequency from 1 Hz to 20 kHz. The lithium electrode-polymer gel electrolyte interfacial stability was evaluated by monitoring the impedance response, using a Solartron 1286/1250 combination, of a cell formed by sandwiching a gel electrolyte between two lithium electrodes. The electrolyte area was 1.85 cm$^2$, and this test was done
in a dry VAC glove box with argon atmosphere with less than 1 ppm of moisture content. X-ray diffraction (XRD) measurements were made using a Philips XRG 3100 X-ray generator equipped with a Ni-filtered Cu-Kα (1.5418 A) source that was connected to a Phillips APD 3520 type PW 1710 diffractometer controller. Scanning Electron Microscopy (SEM) (JEOL JSM 840) was done on gels fractured after freezing with liquid nitrogen. A transmission electron microscope (JEOL 1200 EX TEM) was also used to investigate the nano-structure and morphology of PMMA/clay nanocomposite gel electrolyte. Ultra-thin samples (ca. 80-100 nm thick) were cut with a MT-7000 ultramicrotome under freezing temperatures. Fourier transform infrared (FTIR) absorption spectra were obtained with a BOMEM spectrometer in the range of 4000-500 cm⁻¹. A 45° prism was used to record the attenuated total reflectance (ATR) spectra. Differential scanning calorimetry (DSC) was performed on a TA Instrument DSC 550 from -140°C to 25°C at a heating rate of 10°C/min.

7.3 RESULTS AND DISCUSSION

7.3.1 X-Ray Diffraction

PMMA-clay nanocomposite synthesized via in-situ polymerization with 5 and 10 wt.% of clay was partially exfoliated and intercalated respectively, as described in [38]. For the partially exfoliated sample, the x-ray plot showed no peak. When the nanocomposite was added to the EC/PC–LiClO₄ mixture, the polymer dissolved, possibly affecting the dispersion of the clay. MMT consists of octahedral aluminate sheets between two tetrahedral silicate layers. The silicate layers rearranged themselves in the gel, which had an intercalated structure with d-spacings of 2.85 and 1.40 nm as shown in
Figure 7.1. Polymer nanocomposites with 5 and 10 wt.% clay formed gels, which contained 1.5 and 3 wt.% clay with respect to the total weight of the gel, respectively. These had intercalated structures (Figure 7.1 curves b and c). The corresponding gel electrolyte without any clay showed an amorphous structure with no x-ray peaks.

![Image of XRD patterns showing d-spacing](image)

Figure 7.1. XRD of PMMA gel electrolytes with clay concentrations of: (a) 0%, (b) 1.5%, and (c) 3.0%

In order to verify that the structure in x-ray pattern was from MMT and not from the lithium perchlorate salt, XRD (not shown) of gels containing 1.5 wt.% clay with salt and without salt were compared. The diffraction curves indicated similar peaks; thus, the structure comes from the clay layers that initially are dispersed in the polymer with an average estimate of 50 nm d-spacing according to TEM for the 5 wt% clay sample [38] or 5 nm for sample with 10 wt% clay. However, after swelling the polymer-clay
nanocomposite in plasticizers, heating and subsequent compression to form a gel, some of the PMMA seems to have been extracted out of the clay layers and the clay contracted together again to form an intercalated structure with a much smaller d-spacing, as Figure 7.2 indicates. Similar behavior was observed when the polymer clay nanocomposite was dissolved in THF, and the gel was then dried. XRD (not shown) indicated again a peak corresponding to 2.6 nm, which demonstrated that for the solvents examined (THF or EC/PC), the clay goes back to its intercalated structure.

![Figure 7.2](image)

Figure 7.2. XRD of intercalated PMMA gel electrolyte with 1.5 wt.% clay (a), and exfoliated PMMA nanocomposite (b) used for preparing the 1.5 wt% clay PMMA nanocomposite gel.

### 7.3.2 FTIR Spectroscopy

FTIR spectra of pure PMMA, and of PMMA gel electrolytes containing 0, 1.5, and 3 wt.% of organophilic clay (C18DMB-MMT) are shown in Figure 7.3. In PMMA,
the C=O symmetrical stretch gives a sharp peak at ~1725 cm⁻¹, asymmetric stretching vibrations of C-O-C bond are identified at ~1240 cm⁻¹ and ~1145 cm⁻¹, absorption of ν(C-O) of the OCH₃ group appears at ~1190 cm⁻¹, and symmetrical stretch of the C-O bond in the C-O-C linkage of PMMA at ~987 cm⁻¹ [37, 41]. In the gel electrolytes, the C=O stretch of PMMA at 1725 cm⁻¹ is visible next to the C=O stretch of EC and PC molecules interacting with each other (1797 cm⁻¹ and 1771 cm⁻¹). These two peaks of EC and PC interaction arise from a splitting of the nondegenerate C=O stretch fundamental of a single molecule (EC or PC) into two components [36]. Bands of PC similar to PMMA are also seen in the region between 1100 cm⁻¹ and 1300 cm⁻¹, but precise assignment of these peaks is difficult [37]. The ν(ClO₄⁻) internal mode of the LiClO₄ shows one peak at approximately 624 cm⁻¹ which is assigned to the free anion which does not interact with the lithium cation. There was no peak around 635 cm⁻¹ which could be considered the contact ion pair. The gels with or without clay had the same peak with no difference except the lower intensity for gel with no clay.

Interaction between EC/PC and the solvated salt are also observed by the appearance of satellite bands at 725 and 903 cm⁻¹ near the ring breathing and ring bending vibrations of the carbonate rings at 715 and 893 cm⁻¹, respectively [36, 42,43]. Figure 7.4 depicts these interactions more clearly by comparing PMMA nanocomposite gel with and without LiClO₄. These satellite bands are caused by a shift of the rings from undisturbed configuration due to the close proximity of the cations [36]. The gels without salt do not present these satellite bands.
Figure 7.3. FTIR spectra of (a) pure PMMA, (b) PMMA-PC/EC-LiClO₄, (c) PMMA-PC/EC-LiClO₄-Clay (1.5wt.%), (d) PMMA-PC/EC-LiClO₄-Clay (3.0 wt.%).

Figure 7.4. FTIR spectra of (a) PMMA-PC/EC-LiClO₄-Clay (1.5wt.%), (b) PMMA-PC/EC-Clay (1.5 wt.%).
The interesting result of Figure 7.3 is that the presence of clay in the polymer, and thus in the electrolyte gel, does not affect the spectra. The only difference was a slight change in the intensity of the spectra of the gel with 1.5 wt.% clay compared with gels containing 0 wt.% or 3 wt.% clay. Therefore, a major change in ionic conductivity is not expected since interactions with the clay seem weak or possibly even non-existent. This is consistent with Bohnke et al. [24, 25] in that the PMMA matrix up to 30 wt.% in a gel electrolyte acts as a stiffener and has very little influence on the conductivity of the electrolyte. Lithium and perchlorate ions can migrate through the solvent domain surrounding the polymer matrix.

7.3.3 Electron Microscopy

Freeze fracture SEM highlights the homogeneity of the films as shown in Figure 7.5 for PMMA gel with no clay and with 1.5wt.% clay, respectively. The SEM for the gel with clay added is distinguished by the presence of white dots representing clay particles in the micrograph. At high magnification, achieved via TEM, it is possible to see mostly intercalated aggregates of approximately 20 nanolayers with d-spacing of 2.85 nm as expected from XRD for these gels. There are also a few partially exfoliated layers randomly dispersed as shown in Figure 7.6 for PMMA gel with 3 wt% clay.
Figure 7.5.a. SEM of PMMA:EC:PC:LiClO4 gel electrolyte without clay.

Figure 7.5.b. SEM of corresponding PMMA nanocomposite gel electrolyte with 1.5 wt.% clay.
7.3.4 DSC

The glass transition temperature was obtained from DSC and is compared to the Tg of the PMMA/clay nanocomposite in Table 7.1. The addition of plasticizers greatly decreases the Tg from polymer to the gel. Even though the clay nanolayer dispersion in the gels (intercalated) may not necessarily be the same as in the polymer nanocomposite (partially exfoliated for 5wt.%), a similar increase in the Tg was observed. This demonstrates the capability of nanoclays to enhance thermal stability.
<table>
<thead>
<tr>
<th>Type of nanocomposite</th>
<th>Microstructure</th>
<th>Tg, °C</th>
<th>Tg, °C of gel electrolytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PMMA</td>
<td>--------</td>
<td>105</td>
<td>-90</td>
</tr>
<tr>
<td>PMMA with 5 wt% C18-MMT partially exfoliated</td>
<td>109</td>
<td>-85</td>
<td></td>
</tr>
<tr>
<td>PMMA with 10 wt% C18-MMT Intercalated</td>
<td>112</td>
<td>-84</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.1. Tg values estimated from DSC for PMMA/clay nanocomposites and for gel electrolytes derived from the nanocomposites.

7.3.5 Conductivity Measurements

Ionic conductivities were measured by analyzing the impedance behavior of the gel electrolytes (1.44 cm²) between blocking electrodes. Figure 7.7 shows the ionic conductivity versus temperature for PMMA gel electrolytes with 0 to 3 wt.% clay. For the gel without clay, room temperature conductivity was $5 \times 10^{-4}$ S/cm, which is similar to the literature value obtained by Appetecchi et al. [27]. As the clay concentration increases up to 1.5 wt.%, the room temperature conductivity slightly increases to a maximum of $8 \times 10^{-4}$ S/cm, and then decreases with 3 wt.% clay to $4.5 \times 10^{-4}$ S/cm.
The overall increase in conductivity due to the clay was not as great as demonstrated with other polymers such as PEO and PAN [14-18], and also with dry plasticized PMMA nanocomposite electrolyte [19] shown in Table 7.2. The latter, by Chen et al., illustrated that the presence of the clay promoted dissociation of the lithium salt which could result in an increase in conductivity of up to $6 \times 10^{-4}$ S cm$^{-1}$ at 30$^\circ$C when 5% clay (with respect to PMMA) was used. Their system was different than the one described here; the PMMA/clay nanocomposite was intercalated rather than partially exfoliated and the PMMA molecular weight was between 15,000 and 20,000, at least an order of magnitude lower than that used in this work. Chen et al.’s electrolyte was formed
by dissolving EC, LiClO₄ and PMMA/clay in acetonitrile and then dried in vacuum. In our work, the PMMA/clay nanocomposite had intercalated or partially exfoliated structure depending on the clay concentration and the gel electrolytes contained both EC (46.5%) and PC (19%) as plasticizers.

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>Ionic Conductivity (S/cm) at each clay concentration with respect to polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>Gel PMMA (this work) @ 35°C</td>
<td>7.6x10⁻⁴</td>
</tr>
<tr>
<td>Dry plasticized PMMA [19] @ 30°C</td>
<td>1.5x10⁻³</td>
</tr>
<tr>
<td>Dry PEO [16] @ 30°C</td>
<td>1x10⁻⁵</td>
</tr>
<tr>
<td>Dry PAN [18] @ 40°C</td>
<td>4.7x10⁻⁹</td>
</tr>
</tbody>
</table>

* Estimated from data.

Table 7.2. Conductivity data versus clay concentration for gel PMMA/clay electrolyte, and also for PMMA/clay dry plasticized electrolyte [19], PEO/clay [16], and PAN/clay [18] electrolytes.

Ionic conductivity varied only slightly with clay content exhibiting a maximum at 1.5% as shown in Figure 7.8. Even with such small changes in conductivity, the conduction mechanism can be investigated. Activation energy, $E_a$, for conduction was calculated similarly to Bohnke et al. [24] by fitting the conductivity with the following equation.
empirical expression, which is related to the Vogel-Tamman-Fulcher (VTF) expression based on the free volume concept:

\[ \sigma T^{1/2} = A \exp (-B/(T-T_o)) \]  

(1)

where \(A\), \(B\) and \(T_o\) are fitted constants. The constant \(A\) is related to the number of charge carriers, \(T_o\) is the ideal glass transition temperature and in this case it is assumed to be equal to the Tg of the electrolyte determined by DSC, and \(B\) is proportional to the activation energy of conduction. In fact, \(E_a\) can be expressed as \(B\) multiplied by \(R\), which is the gas constant. When no clay was present, \(E_a\) was similar to the value of 5.4 kJ/mole reported for PMMA-PC-LiClO\(_4\) gel electrolyte [24]. The increase in clay content up to 1.5 wt.% decreased \(E_a\) by 16%, while 3 wt.% increased \(E_a\) by 4% as shown in Figure 7.9.

The slight increase in conductivity at concentration of 1.5% clay can be due to the presence of few clay sheets well dispersed in the matrix besides the intercalated ones as observed by XRD. Since the polymer/clay system at that concentration is only partially exfoliated, some layers during the addition of plasticizers may have maintained their dispersed state. The presence of these clay sheets can provide extra dissociation of the lithium salts. Thus, some lithium cations may interact with the C=O group in the PMMA and increase the amount of free anions, in a similar fashion as described in reference [19], leading to a slight increase in conductivity. However, this interaction must be extremely weak since FTIR could not detect any change in the \(\nu(\text{ClO}_4^-)\) peak for gels with and without clay. At higher clay content, the clay is intercalated [38,39], even in the polymer/clay nanocomposite offering much less interaction than the 1.5% clay system.
Figure 7.8. Conductivity at 35°C of PMMA gel electrolyte as a function of clay content with error bars showing.

Figure 7.9. Activation energy for conduction calculated for PMMA gel electrolyte as a function of clay.
7.3.6 Chemical Stability

Electrochemical stability of the polymer electrolyte in contact with the electrode material is an essential parameter for providing satisfactory performance in a rechargeable battery device. In order to determine the interfacial stability of the PMMA nanocomposite gel electrolyte, impedance measurements were done in a Li-electrolyte-Li type cell, for a period of 21 days. Figure 7.10 shows the time evolution of the interfacial resistance of lithium metal electrode in contact with the gel electrolyte. The PMMA nanocomposite gel electrolyte shows a stable resistance, which is similar to PMMA gel. Thus, in the presence of clay, the interfacial stability is maintained for long periods, i.e. 3 weeks. The ionic conductivity of the samples (not shown) also remained stable during these storage experiments. Similar results for the interfacial resistance of PMMA/EC-PC/LiClO$_4$ gel electrolyte without clay have been obtained by Appetecchi et al. [27] and Ostrovskii et al. [28]. For other clay nanocomposite gels in the literature, the interfacial stability was not reported. However, in other types of electrolytes such as in PAN-based gels, the interfacial resistance continuously increased with time [27] indicating a growth of a resistive layer on the lithium electrode surface, which is a product of the corrosion reaction of lithium with electrolyte components. Thus, PMMA based electrolytes are less reactive towards lithium electrode in comparison with other polymers such as PAN, and a more favorable passivation film grows on the electrode surface [28]. Another sign of interfacial stability was that the lithium surface was still shiny, like new in fact, when the sandwich assembly was opened up at the end of the three-week storage. This demonstrates the excellent interfacial stability of the PMMA clay nanocomposite gels.
Figure 7.10. Interfacial resistance $R_i$ of the lithium electrode in contact with PMMA gel electrolyte with 1.5 wt.% clay and without clay.

7.4 CONCLUSIONS

Using high molecular weight PMMA/clay nanocomposite reported by the authors previously, nanocomposite gel electrolytes were synthesized consisting of PMMA/clay – EC/PC – LiClO$_4$. XRD indicated intercalated structure with d-spacings of 2.85 and 1.40 nm. On addition of the plasticizer to form a gel electrolyte, the clay galleries shrink indicating intercalation rather than the partial exfoliation observed in the PMMA/clay nanocomposite. Ionic conductivity varied slightly and exhibited a maximum value with clay content. The room temperature conductivity for gel without clay was $5 \times 10^{-4}$ S/cm, while for gel with overall clay concentration of 1.5 wt.% the conductivity was $8 \times 10^{-4}$ S/cm, and decreased to $4.5 \times 10^{-4}$ S/cm with 3 wt.% clay. This is because the clay layers
are mostly trapped inside the polymer matrix and, as shown by FTIR, the polymer does not interact with the salt, LiClO$_4$. The presence of clay increased the glass transition temperature of the gel, as determined by DSC. The PMMA nanocomposite gel electrolyte shows a stable lithium interfacial resistance over a three-week storage time, similarly to PMMA gel. Moreover, the lithium surfaces remain perfectly shiny over this period. This stability is a key factor for use in electrochemical applications.

7.5 REFERENCES


CHAPTER 8

CONCLUSIONS AND FUTURE WORK

8.1 HIGHLIGHTS AND CONCLUSIONS

Polymer/clay nanocomposites have been the focus of extensive research in the past decade, in which the polymer matrix contains nano-scale dispersion of the silicate layers. These materials have already been used in commercial applications such as automotive and packaging. It would not be surprising to see a broader range of application for these nanocomposites in the next few years, including storage tanks, flame retardant materials, tires, and others.

This dissertation focused on the synthesis of rubber/clay nanocomposites via mechanical mixing and correlating the enhancements of properties to their nanostructures. In the case of SBR nanocomposites, montmorillonite (MMT) functionalized with four different types of surfactant was used: commercially available octadecyl amine (C18amine) and laboratory synthesized octadecyldimethyl betaine (C18DMB), vinylbenzyl-dodecyldimethylammonium chloride (VDAC), and vinylbenzyl-octadecyldimethyl ammonium chloride (VODAC). The surfactant chain length and functional groups affected the dispersion of clay nanolayers in the matrix and the overall properties of the nanocomposites. X-ray diffraction revealed peaks corresponding to intercalated structures for all system; however, with transmission electron microscopy, partial exfoliation was also observed for samples with long chain surfactants. SBR/VODAC-MMT had highest level of exfoliation and highest aspect ratio in comparison with other nanocomposites. Considerable mechanical reinforcement was
achieved over pure rubber. In particular, for the SBR/VODAC-MMT system: tensile strength and elongation at break increased by more than 3 times that of SBR to reach values of 12.3 MPa and 602%, respectively with only 6 wt.% of silicate. Similar improvements were also observed in the dynamic properties (i.e. elastic modulus). The most significant and unique result was the reduction in oxygen permeability by 60% with the addition of 15 wt.% inorganic filler for SBR/VODAC-MMT. Nanocomposites containing functionalized clay with surfactants of shorter chain (VDAC) or different functional groups (C18DMB, or C18amine) showed permeability reduction by 36%, 49%, and 55% respectively. SBR containing unmodified MMT at the same concentration showed poor reduction in permeability, only 24%. The best performance of nanocomposites containing VODAC-MMT is attributed to the presence of the vinyl-benzyl group in the surfactant which provides higher compatibility with SBR and greater dispersion of the organoclay, increasing the tortuous path for gas diffusion through the rubber.

Furthermore, the effects of carbon black on SBR and on SBR/clay nanocomposites were investigated. While carbon black alone (40 phr) offered great improvement in the mechanical properties of the rubber, the synergism of organoclay and carbon black brought similar property enhancements but at half the total filler loading (10 phr each filler). Also, SBR nanocomposites with the two fillers had good barrier property in comparison with compound containing only carbon black. The morphology appeared to be intercalated with some partial exfoliation of the silicate layers observed by TEM. These unique results indicate that nanocomposites containing organoclay and carbon
black can be a substitute for carbon black filled rubber and offer similar, if not better, performance in tires or other applications.

Two other types of rubber – natural rubber (NR) and bromo-butyl rubber (Br-IIR) – were used in the synthesis of rubber/clay nanocomposites. In the case of natural rubber, oxygen permeability was reduced the most (by 37%) with 10 phr C18DMB-MMT in comparison to nanocomposites containing VODAC-MMT and C18amine-MMT. NR/C18DMB-MMT was intercalated and the clay layers were aligned perpendicular to the gas diffusion direction. For NR/C18amine-MMT, the nanolayers were randomly dispersed reducing the tortuosity of the filler, and for intercalated NR/VODAC-MMT the d-spacing was lower than the others. In the case of bromo-butyl rubber, Br-IIR/C18amine-MMT showed no x-ray diffraction peaks and was almost 3 times stronger than intercalated Br-IIR/VODAC-MMT. Both nanocomposites had similar oxygen permeability: 25% lower than pure rubber for 7.5 phr organoclay content.

Besides rubber/clay nanocomposites, a nanocomposite gel electrolyte was synthesized consisting of poly(methyl methacrylate) (PMMA)/clay, ethylene carbonate (EC) / propylene carbonate (PC) as plasticizer, and lithium perchlorate (LiClO₄). Ionic conductivity varied slightly and exhibited a maximum value with clay content. The room temperature conductivity for gel without clay was 5x10⁻⁴ S/cm, while for gel with overall clay concentration of 1.5 wt.% the conductivity was 8x10⁻⁴ S/cm, and decreased to 4.5x10⁻⁴ S/cm with 3 wt.% clay. The PMMA nanocomposite gel electrolyte shows a stable lithium interfacial resistance over a three-week storage time. This stability is a key factor for use in electrochemical applications.
8.2 FUTURE WORK

One of the main goals in this project has been to increase the level of exfoliation. Different approaches were applied: the use of different specialty surfactants, different mixing conditions, and use of solvent to swell the rubber during mixing. In the mixing process of rubber/clay nanocomposite, the Brabender mixer is heated to 90°C, but heat could not be applied in the 2-roll mill. One suggestion is to use a 2-roll mill with heat in order to facilitate the mixing and dispersion of the clay since the viscoelasticity of the rubber will decrease. Along these changes in the mixing step, process oil (commonly used in rubber mixing) could be added in which the clay is initially dispersed in the oil, and the oil is then mixed with the rubber. Such approach may enhance the clay dispersion in the rubber. The drawback is the decrease in mechanical properties due to the oil, but this could be offset if the nano-layers are more exfoliated than in the present case.

Another suggestion is the study of the Payne Effect in the rubber/clay nanocomposites. In this study, the modulus of the rubber is measured as a function of strain at a constant temperature. In the case of the unfilled compound, the modulus does not change significantly upon increase of strain amplitude, but for a filled rubber, a typical non-linear behavior is observed and is usually termed Payne Effect. This effect is strongly related to the filler network formed in the matrix, and could be used to quantify the filler network in rubber/clay nanocomposites when compared to rubbers filled with carbon black or silica.

A few other measurements/tests could be done in the rubber/clay nanocomposites including crosslinking density and bound rubber content. Measuring the crosslinking density can indicate if the surfactant is influencing the vulcanization process. While, a
rough attempt was done for SBR/VODAC-MMT which showed an increase in the crosslinking density up to 10 phr, these measurements should be carefully done. The same applies to measurement of bound rubber. Bound rubber can be measured prior to vulcanization and is an indication of how much rubber content is physically or chemically bound to the filler. These two tests can help understand the compatibility of the organoclays to the rubber and their effect on the vulcanization process and subsequent effect on the properties of the nanocomposites.

The modeling of the gas transport through rubber clay nanocomposites is a fertile area that needs further development. In this thesis, the morphologies of the clay layers were characterized and are known as well as their orientation in the matrix (from TEM micrographs). One method may be the use of Finite Element Modeling to describe representative volume elements of the nanostructure of the nanocomposite. This may allow for the prediction of the approximate aspect ratio of the fillers.
APPENDIX

The cross-linking density of SBR/clay nanocomposites was measured using the customary swelling technique. This approach measures the dry weight of the sample and the final weight after it is immersed in a solvent for 3 days. The solvent used was chloroform. After determining the swelling capacity, one can calculate the cross-linking density using the Flory-Rehner equation [1]:

\[ \nu = \frac{1}{V_s} \ln(1-V_r) + V_r + \chi V_r^2 \left( V_r^{1/3} \right) \]

Where \( V_s \) is the molar volume of the swelling solvent, \( \chi \) is the polymer-solvent interaction parameter, \( V_r \) is the volume fraction of polymer in a swollen network, and \( \nu \) is the network crosslink. The results are shown in Figure A.1. The cross-linking density increases with VODAC-MMT up to 10 phr and decreases at higher loading. The increase is expected due to the interaction of the surfactant with the rubber during the curing process. The increase is significant but small (<15%). The amine group accelerates the sulphur curing in SBR, which can lead to increase in cross-links. With VDAC-MMT, the cross-linking density appears slightly higher than SBR. The interesting results are for samples with C18amine-MMT and C18DMB-MMT since the cross-linking density decreased with increase in the filler content. This decrease in cross-linking density is unusual, since reports in the literature [2, 3] have indicated that the cross-linking density actually increases in the presence of modified clay with amine containing surfactants. These measurements should be redone possibly with another method to clarify these results.
Figure A.1. Cross-linking density of SBR/clay nanocomposites as a function of clay content.

The TGA curves for the nanocomposites show unique behavior about the thermal degradation of nanocomposites. SBR/organoclay nanocomposites have showed lower degradation temperature than the pure rubber for 20 wt.% decomposition. This behavior is totally opposite of what is observed and reported in the literature about the thermal degradation of nanocomposites. Commonly, the well-dispersed clay layers retard the thermal degradation; this was the case for PMMA/clay nanocomposites which had an increase of 40°C or higher over for sample containing 10 wt.% clay versus pure polymer [4]. Also, the temperature at maximum degradation (Tmax) was higher for SBR and decreased with the clay content. These results are shown in Table A.1 and Figure A.2. For samples containing untreated clay, the temperature at 20% decomposition actually increased with clay content, and the Tmax was similar to SBR.
<table>
<thead>
<tr>
<th>Rubber</th>
<th>Temperature (ºC) at 20 wt.% decomposition</th>
<th>wt.% residue after complete degradation</th>
<th>Rate of degradation at $T_{max}$ (%/ºC)</th>
<th>$T_{max}$ (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>432.92</td>
<td>5.50%</td>
<td>1.212%/ºC</td>
<td>493.36ºC</td>
</tr>
<tr>
<td>SBR + 10 phr VODAC</td>
<td>428.41</td>
<td>11.07%</td>
<td>1.031%/ºC</td>
<td>491.06ºC</td>
</tr>
<tr>
<td>SBR + 20 phr VODAC</td>
<td>428.44</td>
<td>15.64%</td>
<td>1.067%/ºC</td>
<td>480.74ºC</td>
</tr>
<tr>
<td>SBR + 30 phr VODAC</td>
<td>429.74</td>
<td>19.34%</td>
<td>1.107%/ºC</td>
<td>479.14ºC</td>
</tr>
<tr>
<td>SBR + 10 phr C18DMB</td>
<td>425.90</td>
<td>11.47%</td>
<td>1.042%/ºC</td>
<td>490.09ºC</td>
</tr>
<tr>
<td>SBR + 20 phr C18DMB</td>
<td>426.90</td>
<td>16.24%</td>
<td>1.110%/ºC</td>
<td>481.25ºC</td>
</tr>
<tr>
<td>SBR + 30 phr C18DMB</td>
<td>427.41</td>
<td>19.27%</td>
<td>1.140%/ºC</td>
<td>472.17ºC</td>
</tr>
<tr>
<td>SBR + 10 phr C18 amine</td>
<td>425.98</td>
<td>11.46%</td>
<td>1.059%/ºC</td>
<td>493.87ºC</td>
</tr>
<tr>
<td>SBR + 20 phr C18 amine</td>
<td>427.71</td>
<td>16.40%</td>
<td>1.021%/ºC</td>
<td>489.58ºC</td>
</tr>
<tr>
<td>SBR + 30 phr C18 amine</td>
<td>428.01</td>
<td>20.32%</td>
<td>1.017%/ºC</td>
<td>483.31ºC</td>
</tr>
<tr>
<td>SBR + 10 phr VDAC</td>
<td>429.95</td>
<td>11.45%</td>
<td>1.076%/ºC</td>
<td>490.18ºC</td>
</tr>
<tr>
<td>SBR + 20 phr VDAC</td>
<td>429.71</td>
<td>16.68%</td>
<td>1.116%/ºC</td>
<td>482.49ºC</td>
</tr>
<tr>
<td>SBR + 30 phr VDAC</td>
<td>429.75</td>
<td>21.07%</td>
<td>1.124%/ºC</td>
<td>472.41ºC</td>
</tr>
<tr>
<td>SBR + 10 phr NaMMT</td>
<td>431.33</td>
<td>13.22%</td>
<td>1.059%/ºC</td>
<td>490.06ºC</td>
</tr>
<tr>
<td>SBR + 20 phr NaMMT</td>
<td>433.83</td>
<td>19.68%</td>
<td>0.9519%/ºC</td>
<td>493.36ºC</td>
</tr>
<tr>
<td>SBR + 30 phr NaMMT</td>
<td>437.72</td>
<td>25.48%</td>
<td>0.9088%/ºC</td>
<td>491.09ºC</td>
</tr>
</tbody>
</table>

Table A.1. TGA analysis for SBR/clay nanocomposites.

Figure A.2. TGA curves for SBR and SBR/VODAC-MMT
The interesting behavior of SBR/clay nanocomposites was also investigated by Sadhu and Bhowmick [5]. Their system was different than the one in this work in two ways: peroxide curing was applied instead of sulfur curing, and samples were mixed with toluene then dried as opposed to the dry melt mixing. The TGA curves show similar trends as reported here: SBR appears to be slightly shifted to higher temperatures than nanocomposites. The calculated rate of degradation was slower for nanocomposites than SBR and their Tmax was similar to pure rubber. However, the activation energy at 5% conversion level was higher for the nanocomposite than the rubber, and the initial degradation temperature is shifted 25°C higher for the nanocomposites. Thus, their nanocomposites were reported to have better thermal stability than SBR [5]. In the case of SBR/VODAC-MMT, activation energy was determined from TGA and shown in Table A.3. Only at 30% decomposition, the activation energy of SBR/VODAC-MMT (10 phr) was higher than for SBR.

<table>
<thead>
<tr>
<th>Rubber</th>
<th>Decomposition</th>
<th>Activation Energy (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>5</td>
<td>92,592.60</td>
</tr>
<tr>
<td>SBR</td>
<td>10</td>
<td>144,232.17</td>
</tr>
<tr>
<td>SBR</td>
<td>20</td>
<td>165,195.68</td>
</tr>
<tr>
<td>SBR</td>
<td>30</td>
<td>171,352.74</td>
</tr>
<tr>
<td>SBR</td>
<td>40</td>
<td>180,093.14</td>
</tr>
<tr>
<td>SBR</td>
<td>50</td>
<td>179,638.01</td>
</tr>
<tr>
<td>SBR + 10phr VODAC-MMT</td>
<td>5</td>
<td>68,008.04</td>
</tr>
<tr>
<td>SBR + 10phr VODAC-MMT</td>
<td>10</td>
<td>123,760.22</td>
</tr>
<tr>
<td>SBR + 10phr VODAC-MMT</td>
<td>20</td>
<td>162,504.92</td>
</tr>
<tr>
<td>SBR + 10phr VODAC-MMT</td>
<td>30</td>
<td>171,995.39</td>
</tr>
<tr>
<td>SBR + 10phr VODAC-MMT</td>
<td>40</td>
<td>171,999.03</td>
</tr>
<tr>
<td>SBR + 10phr VODAC-MMT</td>
<td>50</td>
<td>164,283.59</td>
</tr>
</tbody>
</table>

Table A.3. Activation energy of SBR and SBR/VODAC-MMT (10 phr).
Only two other papers have observed a reduction in thermal stability for polymer/clay nanocomposites. Bharadwaj et al. [6] observed that the onset of degradation was hastened upon addition of clay to the polyester nanocomposites as compared to pure polymer. The increase in the rate of degradation was speculated to be from the presence of increasing amount of hydroxyl groups in the organic modifier, which provides a supply of oxygen. In our case, the surfactants used do not have the hydroxyl groups. In the other report by Chang et al. [7] the initial degradation temperature (at 2% weight loss) decreased with clay content in poly(lactic acid) (PLA) nanocomposites. In their case, they reference Ogata et al. [8] who reported that the clay seemed to hinder the deformation of the crystalline structures of PLA hybrids at low temperature, but also acted as deformation accelerators at high temperature. In our case, because the surfactant present in between the clay layers starts to decay around 300°C, there is a possibility that the presence of the surfactant is leading to a faster decomposition, while this is not observed in the case of untreated MMT.

Also, TGA analysis (Table A.4) was done for samples containing carbon black and both carbon black and organoclay. Samples containing carbon black show increase in decomposition temperature. When organoclays are present, the decomposition temperature decreases.
Rubber | Temperature (ºC) at 20 wt.% decomposition | wt.% residue after complete degradation  
--- | --- | ---  
SBR | 432.92 | 5.50%  
SBR + 10 phr Carbon Black | 434.92 | 13.04%  
SBR + 5 phr CB +10 phr VODAC-MMT | 427.74 | 14.17%  
SBR + 10 phr CB +10 phr VODAC-MMT | 427.39 | 17.58%  
SBR + 20 phr CB +10 phr VODAC-MMT | 432.14 | 23.40%  
SBR + 10 phr CB +10 phr C18DMB-MMT | 427.48 | 17.63%  
SBR + 20 phr Carbon Black | 437.42 | 19.93%  
SBR + 40 phr Carbon Black | 445.18 | 30.56%  

Table A.4. TGA analysis for SBR containing carbon black and a mixture of carbon black and organoclay.

In the case of NR/clay nanocomposites a similar behavior to SBR/clay nanocomposites was observed: decomposition temperature decrease for systems. For the rubber filled with untreated MMT, the decomposition temperature increased, as shown in Table A.5. In the case of Br-IIR/clay nanocomposites, the decomposition temperature increased in comparison to pure rubber (Table A.6).

Rubber | Temperature (ºC) at 20 wt.% decomposition | wt.% residue after complete degradation  
--- | --- | ---  
NR | 389.52 | 5.72%  
NR + 10 phr VODAC | 389.11 | 11.45%  
NR + 10 phr C18DMB | 387.66 | 11.24%  
NR + 10 phr C18amine | 388.85 | 10.98%  
NR + 10 phr NaMMT | 395.58 | 13.74%  

Table A.5. TGA analysis for NR/clay nanocomposites.
<table>
<thead>
<tr>
<th>Rubber</th>
<th>Temperature (°C) at 20 wt.% decomposition</th>
<th>wt.% residue after complete degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-IIR</td>
<td>407.38</td>
<td>4.16%</td>
</tr>
<tr>
<td>Br-IIR + 7.5 phr VODAC</td>
<td>412.36</td>
<td>9.04%</td>
</tr>
<tr>
<td>Br-IIR + 7.5 phr C18amine</td>
<td>410.30</td>
<td>9.13%</td>
</tr>
</tbody>
</table>

Table A.6. TGA analysis for Br-IIR/clay nanocomposites.


BIBLIOGRAPHY


