Processing, Optimization And Characterization Of Fire Retardant Polymer Nanocomposites

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PROCESSING, OPTIMIZATION AND CHARACTERIZATION
OF FIRE RETARDANT POLYMER NANOCOMPOSITES

by

JINFENG ZHUGE
B.E. Northwestern Polytechnical University, 2008

A thesis submitted in partial fulfillment of the requirements
for the degree of Master of Science
in the Department of Mechanical, Materials, and Aerospace Engineering
in the College of Engineering and Computer Sciences
at the University of Central Florida
Orlando, Florida

Spring Term
2010
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ABSTRACT

Fiber reinforced polymeric composites (FRPC) have superior physical and mechanical properties, such as high specific strength, light weight, and good fatigue and corrosion resistance. They have become competitive engineering materials to replace conventional metallic materials in many important sectors of industry such as aircraft, naval constructions, ships, buildings, transportation, electrical and electronics components, and offshore structures. However, since FRPC contain polymer matrix, the polymer composites and their structures are combustible. FRPC will degrade, decompose, and sometimes yield toxic gases at high temperature or subject to fire conditions.

The objective of this study is to design and optimize fire retardant nanopaper by utilizing the synergistic effects of different nanoparticles. A paper-making technique that combined carbon nanofiber, nanoclay, polyhedral oligomeric silsesquioxanes, graphite nanoplatelet, and ammonium polyphosphate into self-standing nanopaper was developed. The fire retardant nanopaper was further incorporated into the polymer matrix, in conjunction with continuous fiber mats, through resin transfer molding process to improve fire retardant performance of structural composites. The morphology, thermal stability, and flammability of polymer composites coated with hybrid nanopaper were studied. The cone calorimeter test results indicated that the peak heat release rate of the composites coated with a CNF-clay nanopaper
was reduced by 60.5%. The compact char material formed on the surface of the residues of the CNF-clay nanopaper was analyzed to understand the fire retardant mechanism of the nanopaper. The financial support from Office of Naval Research is acknowledged.
To my parents: Zhenhua Zhuge & Genny Hong
ACKNOWLEDGMENTS

I would like to thank Professor Jihua Gou who directed my graduate research and provided me with a great opportunity to access the world of nanocomposite materials. He is an intelligent and energetic research professor. I also wish to acknowledge the help of Dr. Yong Tang, without him, it would have been impossible to accomplish this thesis. I wish to express my appreciation to James McKee who provided generous help and advice for my experiments and thesis writing. My appreciation also goes to Jeremy Lawrence who lended a hand to my experiments during my busiest days.

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CHAPTER 1
INTRODUCTION

1.1. Motivation

1.1.1. Development of composite materials

According to Merriam-Webster, a composite material (or simply composite) is a solid materials which is composed of two or more substances having different physical characteristics and in which each substance retain its identity while contributing desirable properties to the whole; especially: a structural material made of plastic within which a fibrous material (as silicon carbide) is embedded. The constitutions of composites are reinforcement and matrix which holds the discrete reinforcement pieces together and provides them with lateral support.

There are many composite materials that created by nature. Such examples include: wood which composed in a form that cellulose fibers in a matrix of hemicelluloses and lignin; or bones, which are composites of soft protein collagen and hard minerals, called apatite; or granite that consisting of quartz reinforcement; or mica, feldspar, etc. However, most of advance composite materials that used in our daily lives are man-made and synthetic. In responding to people’s requirements, those man-made composite materials show very unique properties such as high specific strength (i.e., high strength-to-density ratio) and extremely
high unidirectional stiffness. In keeping with traditional composites, the attractive combination of high strength and toughness is not possible for any of the single component material. While the use of synthetic materials in the composites is new, examples of composite materials throughout human history are abundant: straw-reinforced mud bricks for construction of huts; laminated bows made from wood, animal tendons, and silk; mud wall with bamboo shoots; concrete reinforced with steel rebar and even concrete itself.

The introduction of fabric reinforced phenolic resins in the 1930s and glass fiber reinforced plastics in the 1940s marks the beginning of the history of modern composite materials development. A steady stream of new composite materials has evolved since. [1] Today, the engineered composite materials in general can be divided into three categories based on the types of matrices, including polymer matrix composites (PMC), metal matrix composites (MMC) and ceramic matrix composites (CMC). While these three categories cover the overwhelming majority of modern composites, there is a newly emerged composite based on carbonaceous matrix called carbon fiber/carbonaceous matrix composites (CCC). In addition to the matrix, one can also define the types of composites based on the geometry of the reinforcement: fiber-reinforced composites, flake reinforced composites and particle-reinforced composites.
The most widely used composite materials are fiber-reinforced composites (FRC) which are composed by fibers of high strength and modulus, embedding into a matrix with distinct interfaces between them. In such a form, both the fiber and matrix retain their individual properties. The combination of the laminate and matrix shows a unique property that cannot be achieved with either acting alone. In the resulting FRC, the matrix works as a medium that keeps the fibers in a desirable direction and location. In this arrangement the fibers serve as the principal load-carrying members, with the matrix transferring the applied forces among the fibers and protecting the fibers from environmental damages such as humidity or chemical corrosion. Consequently, the matrix will also provide many useful functions for the fibers, even though the objective of incorporating fibers into matrix is to enhance the mechanical properties of matrix. [2] The fibers that can be made into FRC are tremendous, including glass fibers, carbon fibers, aramid fibers, extended chain polyethylene fibers, natural fibers, boron fibers and ceramic fibers. The matrix can be chosen from polymers, metals and ceramics. The
wide variety of reinforcements and matrices allows the designer of composite materials to choose an optimum combination. As a result, FRC obtains at least six engineering advantages:

1. The weight is reduced due to the high specific strength ($\sigma_{ult}/\rho$) and high specific stiffness ($E/\rho$).

2. The chemical stability of some matrices makes FRC resisted to acid and alkali.

3. The internal damping property of FRC such as Kevla fiber/epoxy composites is high because of the high impact resistant of the composites.

4. Since the thermal coefficient ($\alpha$) value of composite materials such as graphite/epoxy composite is very low (0.02$\mu$m/m/$^\circ$C compare to steel with 11.7 and aluminum with 23), they exhibit high stability when exposed to extreme mechanical, environmental conditions.

5. Tailor-able property of FRC can be achieved by choosing appropriate combination of reinforcements and matrices or choosing the fiber orientation and lay up sequences such as shown in figure 3.

Figure 2 Comparisons of specific strength of composites with traditional materials. (source from Xia)
Because of these unique mechanical advantages, composite materials are being considered for replacing the traditional metallic materials and are commonly found in many sectors such as aircraft, military, space, automotive, sporting goods, marine, infrastructure and biomedical field. According to a commercial report, the worldwide annual composites market growth at a pace of 4 percent, from about $80 billion USD in 2008 to almost $110 billion in 2013. Globally, the market shared by the so-called BRIC (Brazil, Russia, India and China) is expected to grow from around 22 percent today to 29 percent in 2013, with China alone representing 23 percent of worldwide market that year. The major contribution of the growth comes from building, construction and automotive industries (especially in China), wind energy market that driven by the combination of government regulations and public opinion and aerospace sectors. [3]

Figure 4 Use of fiber-reinforced polymer composites in 787 Dreamliner. (seattlepi.com)
1.1.2. The challenges that encountered by composites researchers

Despite the exciting opportunities that are created by new composite materials, the challenges are numerous. One of the common shortcomings of advanced composite materials is their high manufacturing cost, which limits their large scale production and market penetration. For example, the prices for the raw materials such as epoxy and carbon fiber are around $8/kg and $45/yard respectively. Only those safety-oriented and luxury industries such as aerospace and sports car industries are currently able to afford such high costs to use advanced composites in a large scale. A second issue is that the materials are relatively complex in their mechanical properties, and thus difficult to analyze. For example, the damage detection in composites is more difficult than in metallic structures due to the different conductivity property of the fibers and matrix, the anisotropy of the materials and the majority of the damages often occur beneath the top surface of laminates. [4] Moreover, because of the more recent development of FRC, the data of long term behaviors such as fatigue and fracture has not been gathered in sufficient quantities to establish standards similar to their metallic counterparts, which might lead to some serious safety issues as the materials are in service in the long-term. The difficulty of attaching is another challenge which sometimes leads to the delamination of the FRC. [5] Some other issues facing the widespread deployment and long-term use of FRC include environmental degradation (many polymer matrices absorb moisture), pollution, and the high flammability of polymeric composites. Unfortunately, it is
nearly impossible to discuss multiple problems in a single paper, the discussion in this thesis is focused on how to improve the fire resistance of fiber-reinforced polymeric composites (FRPC) when the organic property i.e. flammability of polymer matrix is concerned.

1.2. Development of Flame Retardant Technology

1.2.1. Fire issues of FRPC

According to a report written by the fire analysis and research division of National Fire Protection Association, in the year of 2008 every 22 seconds a fire department responds to a fire somewhere in the country. A fire occurs in a structure every 61 seconds, and one in a residential structure occurs every 78 seconds. Additionally, a fire occurs in a vehicle every 134 seconds, and there is a fire in an outside property every 45 seconds. As a result, there were 3,320 recorded deaths in 2008, which equates to one every 158 minutes. In the same year a fire-related injury was reported every 31 minutes, leading to 16,705 fire-related injuries. An estimated $15,478,000,000 in property damage occurred as a result of fire in 2008. [6] Additionally in 2008, 118 firefighters were reported to be lost in the line of duty. [7] It seems that the United States is one of the highest fire loss rates countries of the industrialized world – both in terms of fire deaths and dollar loss. Five important factors appear to place the nation in such a situation: (1) the country spends relatively little fire prevention activities; (2) the tolerance for “accidental” fires, i.e. a blaze with no fatalities or injuries, is greater than other
countries; (3) compared with people in other countries, Americans practice riskier and more careless behavior, such as the use of space heaters; (4) the houses built in this country are not with the same degree of fire safety in mind; (5) the most importantly thing is Americans tend to have more personal belongings in the home, which means more ignition sources and fire load.[8] It is impossible to truly solve all the problems in one shot, but what researchers can do is find and attempt to overcome as many of the major causes as possible. As mentioned earlier, polymeric materials are becoming the major materials used to make the tools, structures, facilities around us (table 1 & 2). [8] Therefore, it is crucial to improve the fire performance of polymeric materials in order to ensure a safety environment for human lives and property.

Table 1 North American Plastic Production-1999 and 2007 (millions of pounds, dry weight basis). (from G.L. Nelson and C.A.Wikie [2007])

<table>
<thead>
<tr>
<th>Resin</th>
<th>1999 Production</th>
<th>2007 Production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>657</td>
<td>642</td>
</tr>
<tr>
<td>Urea and melamine</td>
<td>2,985</td>
<td>3,471</td>
</tr>
<tr>
<td>Phenolics (gross wt)</td>
<td>4,388</td>
<td>4,838</td>
</tr>
<tr>
<td>Total Thermosets</td>
<td>8,030</td>
<td>8,951</td>
</tr>
<tr>
<td>LDPE</td>
<td>7,700</td>
<td>7,927</td>
</tr>
<tr>
<td>LLDPE</td>
<td>8,107</td>
<td>13,584</td>
</tr>
<tr>
<td>HDPE</td>
<td>13,864</td>
<td>18,222</td>
</tr>
<tr>
<td>PP</td>
<td>15,493</td>
<td>19,445</td>
</tr>
<tr>
<td>ABS</td>
<td>1,455</td>
<td>1,270</td>
</tr>
<tr>
<td>Other Styrenes</td>
<td>1,767</td>
<td>1,726</td>
</tr>
<tr>
<td>PS</td>
<td>6,471</td>
<td>6,015</td>
</tr>
<tr>
<td>Nylon</td>
<td>1,349</td>
<td>1,295</td>
</tr>
<tr>
<td>PVC</td>
<td>14,912</td>
<td>14,606</td>
</tr>
<tr>
<td>Thermoplastic Polyester</td>
<td>4,846</td>
<td>8,745</td>
</tr>
<tr>
<td>Total Thermoplastics</td>
<td>75,964</td>
<td>92,835</td>
</tr>
<tr>
<td>All Other Resins</td>
<td>13,467</td>
<td>14,007</td>
</tr>
<tr>
<td>Grand Total</td>
<td>97,461</td>
<td>115,793</td>
</tr>
</tbody>
</table>

Notes: *US, Canada and Mexico as noted, †Canada Included, ‡Mexico Included
1.2.2. The history of fire retardants

Humanity has a long history that of endeavors in making normally flammable materials fire resistant. Herodotus of Halicarnassus, a Greek historian who lived in the 5th BC recorded in his book that Greek people used aluminum potassium sulfate (KAl(SO₄)₂·12H₂O) as paints or coatings for wood to improve its fire resistance. About 200 years later, the Romans improved this technology by adding vinegar into KAl(SO₄)₂·12H₂O solution. Later on, they applied their fire resistant inventions into military field. In the 17th century of Germany, canvases were treated with a mixture of clay and gypsum, which was called “inflammable canvas,” this canvas was also widely used as curtain in theaters. [9]

---

Table 2 Resins Sales By Major Markets (millions of pounds).
(from G.L. Nelson and C.A.Wike [2007])

<table>
<thead>
<tr>
<th>Major Market</th>
<th>2007</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transportation</td>
<td>3,312</td>
<td>4.0</td>
</tr>
<tr>
<td>Packaging</td>
<td>26,527</td>
<td>32.2</td>
</tr>
<tr>
<td>Building &amp; Construction</td>
<td>14,289</td>
<td>17.4</td>
</tr>
<tr>
<td>Electrical/Electronic</td>
<td>1,980</td>
<td>2.4</td>
</tr>
<tr>
<td>Furniture &amp; Furnishings</td>
<td>3,091</td>
<td>3.8</td>
</tr>
<tr>
<td>Consumer &amp; Institutional</td>
<td>17,193</td>
<td>20.9</td>
</tr>
<tr>
<td>Industrial/Machinery</td>
<td>943</td>
<td>1.1</td>
</tr>
<tr>
<td>Adhesives/Inks/Coatings</td>
<td>1,069</td>
<td>1.3</td>
</tr>
<tr>
<td>All Others</td>
<td>1,604</td>
<td>1.9</td>
</tr>
<tr>
<td>Exports</td>
<td>12,346</td>
<td>15.0</td>
</tr>
<tr>
<td><strong>Total Selected Plastics</strong></td>
<td><strong>82,354</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

Note: ^Data for ABS, SAN, Other Styrene-Based Polymers, and Engineering Resins are not included.
The first patent for flame retardant technology was issued to British scientist Obadiah Wyld in 1735 and was considered as an important milestone in the history of flame retardants. The first scientific exploration of controlling flammability was carried out by Joseph Louis Gay-Lussac in 1821. It was not until the year of 1913, the famous chemist William Henry Perkins developed the ground work for the flame retardant theory. [10] He was the first person to study the mechanism of flame retardancy on wood, cotton, paper and plastics. Unfortunately, his work was not widely appreciated during that time and the developments of fire retardant technology remained stagnant until Second World War. [9]

Between 450 B.C. and the early 20th century, most of additives and fillers that used to reduce the flammability of different materials were inorganic by nature. Such examples include the mixtures of alum and vinegar; clay and hair; clay and gypsum; alum, ferrous sulfate, and gypsum; and ammonium chloride, ammonium phosphate, borax, and various
acids. The objectives of those early attempts are mainly focused on reducing the flammability of wood for military materials, theater curtains, and other textiles. [11]

1.2.3. Development of flame retardant technology for polymers

In the 1950’s, the polymer industry started to grow into a big market and the fire retardant research entered a new era. It quickly became obvious that the inorganic flame retardants developed over centuries have a very limited effect on reducing the flammability of the hydrophobic polymers that were rising in popularity. As such, the development in fire retardant technologies after WWII and until now was focused on the flame retardants that were compatible with polymers. The achievements during this period were remarkable. [9] For instance, the successful developments of durable flame retardant textiles were recognized by Du Pont’s Erifon, Tianium Pigment’s Titanox FR and products from American Cyanamid. Besides that, the applications of halogen-antimony synergism flame resistant systems had been considered as a milestone in the field of flame retardant chemistry. Although today the applications of halogen based flame retardants are limited due to the environmental and healthy issues; however, it is still one of major additives to control the flammability of polymers in real world applications. The mechanism of this flame retardant is that the halogen radicals can retard the flame effectively by acting quickly as a radical trap, capping the high energy free radicals HO· and H· in the vapor phase.
H· + HX → H₂ + X·

HO· + HX → X· + H₂O

X· + RH → HX + R·

X= Cl or Br

Furthermore, the product HX, such as HBr and HCl are nonflammable and in gas phase, which creating a protective gas layer above the condensed phase to stop further combustion of polymer. By the addition of antimony oxide (Sb₂O₃) the effective of the halogen radicals will be further enhanced. Antimony oxide serves as synergist, improving the activity of the halogenated additives which in term lower the amount of additives that are needed. As shown in the following chemical equations, antimony oxide acts as a halogen shuttle bringing SbX₃ into the vapor phase. [12]
\[
R\text{-HX} \rightarrow R + \text{HX} \quad (\sim250 \, ^\circ\text{C})
\]
\[
2\text{HX} + \text{Sb}_2\text{O}_3 \rightarrow 2 \text{SbOX} + \text{H}_2\text{O} \quad (\sim250 \, ^\circ\text{C})
\]
\[
\begin{align*}
5 \text{SbOX}(s) & \rightarrow \text{Sb}_4\text{O}_5\text{X}_2(s) + \text{SbX}_3(g) \quad (245-280 \, ^\circ\text{C}) \\
4 \text{Sb}_4\text{O}_5\text{X}_2(s) & \rightarrow 5 \text{Sb}_3\text{O}_4(s) + \text{SbX}_3(g) \quad (410-475 \, ^\circ\text{C}) \\
3 \text{Sb}_3\text{O}_4(s) & \rightarrow 4 \text{Sb}_2\text{O}_3(s) + \text{SbX}_3(g) \quad (475-565 \, ^\circ\text{C})
\end{align*}
\]
\[
\text{Sb}_2\text{O}_3(s) \rightarrow \text{Sb}_2\text{O}_3(l)
\]
\[
\begin{align*}
\text{SbX}_3 + \text{H} & \rightarrow \text{SbX}_2 + \text{HX} \\
\text{SbX}_2 + \text{H} & \rightarrow \text{SbX} + \text{HX} \\
\text{SbX} + \text{H} & \rightarrow \text{Sb} + \text{HX}
\end{align*}
\]

Some commercially available halogenated additives are similar poly brominated biphenyls (PBB) as seen in figure 6. [13]

Figure 6 Commercially available halogenated additives. (from J.L. Jurs [2007])

Another successful achievement for flame retardants was development of reactive flame retardants to improve the fire performance of polyesters. The retardants are connected to the unsaturated polyester at the final stage of synthesizing polyester resin, permitting the materials long lasting fire retardancy property. [9] As a result, the chemical leakage appears
among the brominated flame retarded polymer would not happen in this case. Such products include Eohoehzehzel, DBS, Tribromophenol, etc.

The invention of intumescent flame retardant systems was another milestone during the development of flame retardant which was inspired by the fact that the limiting oxygen index (LOI) of carbon is extremely high (about 65%). The word “intumescent” was first used by Olsen and Bechle in 1948 to describe the phenomenon of swells as a result of heat exposure.

The molecule of an intumescent fire retardant is composed by Acid Source, Carbon Source and Foaming Source. As shown in figure 7, during combustion process, the foaming source of the flame retardant can cause the whole material foam up and the carbon source decomposes into carbon based char, protecting underlying structure by inhibiting mass and heat flow. Moreover the acid source of the flame retardant will act as catalyst to stimulate the pyrolysis of polymer into char. A typical intumescent flame retardant which has been widely used is the ammonium polyphosphate (APP).[9] Compare to the halogenated flame retardants, IFR is growing rapidly as people concern more about environmental and healthy issues since 1980s.

![Figure 7 Intumescent residue after LOI test of an intumescent poly(propylene).](image)
Halogenated compounds have negative environmental impact and also are highly toxic when burning, which have deterred many countries from using them. [14] In addition, halogenated organic compounds are considered Persistent Organic Pollutants that are not easily broken down or oxidized. As a result, Polychlorinated biphenyls (PCBs) were banned in 1977, and with the evidence that the chemicals could accumulate in human breast milk, the EU had banned several types of brominated flame retardants in 2008. The same year, many states in USA and various other countries were investigating the potential dangers of polybrominated diphenyl ethers (PBDEs). Last year, the U.S. National Oceanic and Atmospheric Administration (NOAA) released a report, claiming in contrast to earlier reports, stating that PBDEs were found throughout the U.S. coastal zone. Moreover, it was noted that more than 80% cases of death in fire were caused by the toxic gas such as dioxins and furans released by pyrolysis of halogenated flame retardants contained in around environment. [15-18] Therefore people also began to seek less dangerous types of flame retardants by switching their attention to aluminum, nitrogen, phosphorous and boron compounds, rather than the intumescent flame retardants. The general mechanism of these types of flame retardants is by diluting both the condensed and vapor phase of the polymer with non-flammable salts, acids and by-products such as water and alumina. Table 3 shows world consumption of flame retardants containing bromine peaked in 1992. However, aluminum containing flame retardant additives overtook the first place in 1996. [13]
Table 3 Global consumption of flame retardants according to base element content. (from J.L. Jurs [2007])

<table>
<thead>
<tr>
<th>Base Element</th>
<th>Market Volume 1992 (t)</th>
<th>Market Volume 1996 (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromine</td>
<td>150,000</td>
<td>202,000</td>
</tr>
<tr>
<td>Chlorine</td>
<td>60,000</td>
<td>50,000</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>100,000</td>
<td>137,000</td>
</tr>
<tr>
<td>Antimony</td>
<td>50,000</td>
<td>70,000</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>30,000</td>
<td>30,000</td>
</tr>
<tr>
<td>Aluminum</td>
<td>170,000</td>
<td>410,000</td>
</tr>
<tr>
<td>Other</td>
<td>50,000</td>
<td>55,000</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>610,000</strong></td>
<td><strong>924,000</strong></td>
</tr>
</tbody>
</table>

*Includes USA, W. Europe, Asia

Besides the approach of incorporating additives into polymer, there is another way to improve the flame resistance of FRPC i.e. intrinsically improve the flame resistant of polymers. These polymers are synthesized as intrinsically fire-resistant show most efficient in resisting the combustion reaction. The intrinsic flame resistant polymers only decompose at elevated temperatures. When developing heat resistant polymers, there are some issues should be considered. First of all, compounds that been used should have strong covalent bonds. Secondly, in order to maximize the bonding energy, the aromatic polymer rings should be resonance stabilized. Moreover, all of the rings in the structure should have no bond strain or weak point. All of the bond angels should be normal. Finally, the most stable ladder polymer which has multiple bonding to several centers should be utilized. [19] Most of intrinsically “inflammable” polymers are made by incorporation of aromatic cycles or hetero-cycles. These types of structures ensure their tendency to decompose into chars upon
combustion which would reduce the amount of flammable gas release and the intensity of external heat radiation. Figure 8 shows the general structures of two types of ladder polymers.

[20]

Figure 8 Two representative structures of different types of ladder polymers. (wikipedia.org)

The left type of ladder polymer links two polymer chains with periodic covalent bonds and the right one is composed by a single double-stranded chain. A remarkable thermal stability is achieved since the chains do not necessarily fall apart if one covalent bond is broken. [20] It is logical to draw the conclusion from the above discussion that the cost of intrinsic flame retardant polymers is relatively high that prevent them from widely applications. There are many polymers that have been developed over the years but few have ever achieved commercial success. The most notably economically feasible intrinsic flame retardant polymers are Kevlar, polyether imides, polyetheretherketone (PEEK) and Teflon (figure9). [13]
1.3. Research Methods

1.3.1. The phenomenon of combustion

In order to design effective flame retardant, it is a privilege to understand the process of combustion reaction, or more specifically, the burning process of polymer. General speaking, there are two kinds of flames: premixed flame where gas and fuel source are kept constant such as oxygen acetylene torch and diffusion flame where the oxygen diffuse into the fuel mixture from the surrounding atmosphere such as the burning of FRPC. [21] The evolving of the diffusion flame, which will be discussed throughout this thesis, has three steps that are necessary and occur in the following order: the heating of the fuel source; followed by decomposition of the fuel source into combustible and non-combustible materials; and finally the ignition of the combustible fuel and air mixture to produce a flame. [10] The decomposition of the fuel source essentially is the breaking of chemical bonds, transforming the fuel into high energy free radicals. This process is initially done by an external heat source. As long as the
combustion process is initiated and the fuel/air mixture remains constant, the heat generated by exothermic combustion of the fuel is enough to keep the flame propagating. The mass transfer of the fuel/air mixture into the pyrolysis zone (figure10) and energy transfer back to the fuel source are crucial to sustain the combustion process. During the combustion process, the oxygen, heating rate and pressure of environment together are playing significant roles. [10][22]

![Combustion process of condensed phases](image)

Figure 10 Combustion process of condensed phases. (courtesy of M.P. Stevens)

1.3.2. Mechanisms of flame retardants in polymers

Once the combustion process is understood, it is possible to plan the strategies to stop the propagation of the fire. When a polymer is under external heat flux, the polymer can decompose to form the high energy free radicals and evaporate. If the concentration of volatile products are sufficient, within the flammability limits and the temperature is above the ignition temperature, the combustion proceeds. [23] Figure11 schematically illustrate the two phase of a burning plastic piece. [20] Accordingly, one can extinguish the fire chemically and
physically in both the vapor phase and condensed phase by controlling the heat and/or fuel below critical level. In the condensed phase, there are two approaches to stop the combustion cycle. Firstly, one can dilute the solid fuel with inorganic fillers (e.g. talc or calcium carbonate). This lowers the combustible portion of the material, ultimately, lowering the amount of heat per volume of material it can produce while burning. Alternatively incorporate additives that would create an endothermic environment when reacting such as magnesium and aluminum hydroxides as well as various hydrates such as hydromagnesite. Secondly, stimulate polymer to form carbonized foaming char (e.g. intumescent additives) which act as a protective layer for both mass immigration and heat radiation. In the vapor phase, the combustion cycle can be stopped by physically diluting the flame with inert gases (such as carbon dioxide and water) produced by thermal degradation of some materials or chemically removing fire-propagating radicals such as H· and OH with halogenated gases (e.g. hydrogen chloride and hydrogen bromide). [10] These specific chemicals can be added into the polymer molecules permanently i.e. intrinsically fire resistant polymers or as additives and fillers i.e. flame retardants.
1.3.3. The ideas adopted to improve the fire performance of FRPC

As discussed in previously, halogenated fire retardants are effective, however they are increasingly being phased out due to growing environmental and health concerns. Meanwhile, the intrinsic flame resistant polymers are currently too expensive to expand their application territories unless a break-through technology emerges that dramatically reduces the cost of synthesizing this type of polymer. Moreover, the amount of traditional additive and filling fire retardants required to mix with aimed polymer to achieve outstanding fire performance are so large that the potential to harm the mechanic properties of composites exists. Yet the large amount of fire retardants requirement also increase the weight as well as the cost of such composites. The endeavor of seeking desirable flame retardant in this thesis is focused on the development of nanotechnologies and nanomaterials.
Due to the boom of nanotechnology, the polymer nanocomposites become the major field of polymer materials research since the early 1990s. Nanocomposites can be made from a wide variety of starting materials such as gases, metals and minerals, giving a range of enhanced properties including electrical conductivity and superparamagnetism as well as fire retardancy. [24] Lots of scientists and groups have done pioneering work regarding to fire retardant nanocomposites such as Takashi Kashiwagi, Charles A. Wilkie, Jeffrey W. Gilman, NIST, Cornell University, etc. Many nanoparticles have been investigated and show exciting flame retardant effects when very little amount is mixed into polymer such as nanoclay, TiO$_2$, silica, layered double hydroxides (LDH), carbon nanotubes (CNT) and polyhedral silsesquioxanes (POSS). [25] Companies including Nanocor and Albemarle Corporation have already applied the laboratorial achievement into real application: nanoclay based flame retardants are used in electronics, wires, cables, and decorative wall papers. [16]

In this thesis, the latest achievements in the explorations of nanoscaled flame retardant are used as references. The strategy of quenching the fire in condensed phase has been adopted and developed. Specifically, carbon nanofibers (PR-25, HHT) are used to fabricate carbon nanofiber papers that work as a structure to hold nanoparticles such as polyhedral silsesquioxanes (POSS), graphite and montmorillonite clay (naturally occurring clay). Then the hybrid papers are coated onto the surface of FRPC during resin transfer molding (RTM) process. The purpose of coating the hybrid nanopaper is that this coat is expected to serve as a “pre-existed protective char” barrier which may form during combustion otherwise.
1.4. The Structure of the Thesis

The following chapters are arranged in such a sequence: During chapter 2, some of the latest developments in nanocomposites research are reviewed. The work of those pioneering scientists will be appreciated and many kinds of nano-sized particles that have been used or have potential to reduce the flammability of FRPC are introduced. From chapter 3 to chapter 5, detailed research work of my own during two years of graduate study are revealed. Specifically, chapter 3 is mainly focused on the exploration of flame resistant mechanism of composite coated with CNF and POSS hybrid paper systems. Also some preliminary research of clay-CNf hybrid system is introduced. Due to the remarkable flame resistant property of CNF-clay hybrid paper showed in chapter 3, a detailed discussion about the synergistic effect between carbon nanofiber, pristine clay and organically modified clay are carried out in chapter 4. In chapter 5, the flame resistant effect of another planar structure particle, i.e. exfoliated graphite nano platelets (xGnP) is examined and discussed. In this chapter, the traditional flame retardant APP is incorporated in to the polymer matrix and the underlining mechanisms of fire resistance are speculated and proved. The last section ended in chapter 6 where the overall fire performance of FRPC coated with pure CNF, CNF/POSS, CNF/clay, CNF/xGnP and pure xGnP nanopapers is compared and discussed. Besides that, future work regarding to flame resistant studies is brought up.
2.1. The New Demands in 21st Century for Flame Retardants

During the proceeding chapter, it is shown that composites materials have attractive advantages in replacing traditional metallic materials in many uses. However, one of the biggest issues is that most composite materials use polymer as their matrix, which greatly increases the potential of catching fire when they are exposed to heat radiation. Many scientists, institutions, and organizations have devoted research into improving the fire performance of polymer composites since the invention of these relatively new materials. Indeed, many great ideas, patents, and products appeared during the past few decades stimulated the extensive application of polymeric composite materials. Today, they have become one of the major engineered materials that in people’s daily lives. Nevertheless, with people becoming more serious about personal health, and the global environment, as well as sustainable development since the beginning of the new century, the traditional approaches to enhance the fire performance of polymeric composites are faced with great challenges. The most effective traditional fire retardants, namely the halogenated additives, are already banned or limited their applications worldwide. Therefore, it is crucial to find new and effective solutions as soon as possible. However, it is impossible to solve such a challenge by
researchers in composites field alone. The demanding for global cooperation and interdisciplinary researches are necessary and inevitable. Thanks to the intensive researches in nanomaterials and nanotechnologies during the past few decades, researchers in fire retardant polymeric composites are inspired and find great opportunities to replace the traditional and toxic flame retardants by adopting new thinking in nanotechnologies.

2.2. A Brief Introduction to Nanomaterials

A salient event in the history of nanotechnology recognized by many scientific historians was the remarkable 1959 talk by Nobel Laureate Richard Feynman at the meeting of American Physical Society at Caltech. [26] In the famous speech, Dr. Feynman foresaw the development of nanomaterials, nanolithography, nanoscale digital storage, molecular electronics and nanomanufacturing methods. Since then the research in nanotechnology was evolving and expanding rapidly as shown in table 4.
In 2001, the Clinton administration raises nanoscale science and technology to the level of federal initiative, officially referring to it as the National Nanotechnology Initiative (NNI) and they define nanotechnology as follows:

*Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nm, where unique phenomena enable novel applications. A nanometer is one-billionth of a meter: a sheet of paper is about 100,000 nanometers thick. Encompassing nanoscale science, engineering, and technology, nanotechnology involves imaging, measuring, modeling and manipulating matter at this length scale. At this level, the physical, chemical and biological properties of materials differ in fundamental and valuable ways from the properties of individual atoms and molecules.*
or bulk matter. Nanotechnology R&D is directed towards understanding and creating improved materials, devices and systems that exploit these new properties. [27]

Recently, funding from large industry, small business, investors as well as Federal, state and local governments for the R&D in nanotechnology is over $2 billion per year, seeking cleaner and less wasteful methods of manufacture, stronger and lighter building materials, smaller yet faster computers, and more powerful ways to detect and treat disease.

Why the nano scale so important? According J.H. Koo’s book published in 2006: materials variations on the nanometer scale will influence the wavelike (quantum mechanical) properties of electrons inside matter and atomic interactions. Therefore it is possible to control the fundamental properties of materials, such as their melting temperature, magnetic properties, charge capacity and even color just by creating different nanometer-scale structures without changing the material’s chemical compositions. As a consequence, high performance products and technologies that were not possible before might be brought out by making use of this potential. [28]

By the virtue of the unique properties of nano-sized materials and the specific performance carried by those materials, nanomaterials and nanotechnologies have already played an important role in many branches. For example, in the cosmetic industry, strong UV protection can be achieved using TiO₂ nanoparticles. If compared to the regular cream, due to the nanosize of particles, they are invisible on the skin even when present in large quantities. Medicine, life sciences and pharmaceutics also benefit from nanotechnologies which for
example may help improve the reception of implants by the body. Moreover, by adopting nanotechnology, the quality of cancer treatment might be greatly improved by allowing the agents to target tumor cells directly without damage the entire organism in the process, see figure 12. [30] Ultra-light yet extremely stable materials would be created by adding nanotubes to plastics, which have huge potential applications in aerospace, automotive sectors…

![Image](image.png)

Figure 12 Cancer Cells before and (right) after the take-up of ironoxide nanoparticles. (courtesy of Sylvia Leydecker)

However, the commercialization of nanoproducts is still at an early stage. Even though, research that focuses on nanomaterials and nanotechnologies is one of the most popular areas. According to the New York business consultancy Lux Research, a total of 12.4 billion US dollars were invested worldwide in research and development in the field in 2006, with nanotechnology-based products already being responsible for a turnover in excess of 50 billion US dollars. 6801 patents about nanotechnologies and nanomaterials were registered in U.S. along with 773 patents in Germany. Furthermore, the Lux Research estimated that the global market volume for nano-based products in 2010 at $500 billion with a projected $2.6 trillion in 2014. In short, nano-based products will become commonplace and achieve major
2.3. Applications of Polymer Nanocomposites

Since the polymer-additive interface is a key determinant of composites properties and the surface to volume and aspect ratios of nanoscale fillers are extremely high, making them ideal for application in polymeric materials. Some simple calculations are proposed by H.C. Ashton to address the subject of the polymer-nanoparticles interface [31]:

- Assume the surface of a 1-μ cube equals 6μ³, for the sake of simplicity.
- The value also equals 6 x 10⁶ nm² if expressed in terms of nanometers.
- The surface of a 1-nm cube equals 6 nm².
- If the 1-μ cube were fractured into 1-nm cubes, the total number of cubes generated would be 10⁹. As a result, the total surface of the new cubes equals 6 x 10⁹ nm².

Therefore, the surface area of the same material increased by 1000 times!!!

Of course, in real life application, the nanosized particle may not necessary as small as 1 nm. However, the size of traditional additives particles may also greater that 1μm, making such a possibility exists. Furthermore, since a size of typical polymer molecule as shown in figure 13 is about 40nm in diameter which is close to the nanofiller’s size, leading very strong Van der Waals force and molecular interaction between polymer and nanosized filler. The particular structures of polymeric nanocomposites have resulted in major improvements in mechanical properties, gas barrier properties, thermal stability, fire
retardancy, electrical properties, etc. However, besides these exciting improvements, there still some disadvantages come along with nanocomposites (table 5). [28] As a consequence, the majority of the research in polymer nanocomposites is focused on how to disperse nanofillers uniformly into matrix and how to modify the surface of nanofillers so that not only the particles can be well distributed but also the desired properties can be achieved and/or enhanced. [32-36]

Table 5 Improvements and disadvantages of nanoparticles to polymers.
(courtesy of J.H. Koo)

<table>
<thead>
<tr>
<th>Improvements</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Mechanical properties (tensile strength, stiffness, toughness)</td>
<td>• Viscosity increase (limits processability)</td>
</tr>
<tr>
<td>• Gas barrier</td>
<td>• Dispersion difficulties</td>
</tr>
<tr>
<td>• Synergistic flame retardant additive</td>
<td>• Optical issues</td>
</tr>
<tr>
<td>• Dimensional stability</td>
<td>• Sedimentation</td>
</tr>
<tr>
<td>• Thermal expansion</td>
<td>• Black color when different carbon containing nanoparticles are used</td>
</tr>
<tr>
<td>• Thermal conductivity</td>
<td></td>
</tr>
<tr>
<td>• Ablation resistance</td>
<td></td>
</tr>
<tr>
<td>• Chemical resistance</td>
<td></td>
</tr>
<tr>
<td>• Reinforcement</td>
<td></td>
</tr>
</tbody>
</table>
To date, there are many commercial nanocomposites have been successfully launched in market. For example: Nanocomposites concentrates are being evaluated in films not only for enhancing barrier, but also to control the release and migration of additives such as biocides; PolyOne commercialized nanocomposites products in the Nanoblend™ family of concentrates and compounds for polyolefin resins. These composites are based on nanoclays and can reduce the amount of mineral fillers, often used as fire retardants that are required in many compounds; RTM has developed nanotube-based thermoplastic composites for the electronics industry in hard disk drive and wafer handling equipment; Honeywell Polymer has developed Aegis TM OX for high-barrier beer bottles and Aegis NC (Nylon 6/barrier nylon) for medium barrier bottles and films…
2.4. A Review of the Flame Resistant Research for Nanocomposites

In the fire retardancy research area, nanoscaled flame retardants showed their environmental compatibility nature when compared to the flame retardants such as halogenated additives. They do not have the common drawbacks come along with other non-halogenated additives. For instance, the addition of nano particles into polymer will not only improve the fire performance of the resulting composite, but these particles would also greatly improve the mechanical, electrical properties of the final products instead of harmful side effects that would typically be found when use traditional additives. Moreover, in order to achieve similar or even better fire performance during bench scale tests, only very small amount of nano particles are required. Besides that, no particular equipments are required to process nanocomposites. Those normal techniques including extrusion, injection molding and casting can also be used. As a consequence, extensive researches of flame resistant nanocomposites have already done with promising results in terms of reduction in peak heat release rate (PHRR) during cone calorimeter test.

HRR is one of the most important parameters to evaluate the flammability of materials which is obtained by conducting cone calorimeter test. A schematic diagram of the instrument is shown in the figure 14. Besides the HRR and PHRR, lots of other useful information can also be obtained from the tests, including the entire heat release rate as a function of time, time to ignition, mass loss rate, production of smoke, CO and CO₂.
The principle of monitoring the HRR during cone calorimeter test shown in figure 14 left is based on the empirical observation by Huggett that almost all the types of fuel would generate 13.1MJ heat of combustion when 1 kg of O₂ is consumed. [37] And the rate of oxygen consumption is readily determined by measuring the concentration of oxygen in the exhaust duct and the volumetric flow of air. As a result, the HRR is given by the following equation:

\[
\dot{q} = (13.1 \times 10^3) \cdot 1.10C \cdot \sqrt{\frac{\Delta P}{T_e}} \cdot \frac{0.2095 - X_{O_2}}{1.105 - 1.5 \cdot X_{O_2}}
\]

Where
- \( \dot{q} \) = Rate of heat release (kW)
- \( C \) = Orifice plate coefficient (kg\(^{1/2}\)m\(^{-1/2}\)K\(^{1/2}\))
- \( \Delta P \) = Pressure drop across the orifice plate (Pa)
- \( T_e \) = Gas temperature at the orifice plate (K)
- \( X_{O_2} \) = Measured mole fraction of O₂ in the exhaust air (no units)

The geometry of nanoparticles that have been dispersed in polymers can be lamellar structure: clays, graphite, layered double hydroxides (LDHs) to list a few examples; or two-dimensional
linear structures such as the well known carbon nanotubes and carbon nanofibers; or three dimensional structures such as polyhedral oligomeric silsesquioxane (POSS). Among those nanosized particles, the fire performance of nanoclay-polymer nanocomposites is the most widely studied. In the late 1940s, polymers that combined with nanoscale layered silicates appeared in a patent application by Carter et al. \[35\] During the early stage of development, a large amount of clay loading (50% mass fraction) was required. The dramatically decreased clay loading (less than 10% mass fraction) polymer nanocomposites were found in patents from General Motors (GM), Imperial Chemical Industries (ICI), and DuPont thirty years later. \[38\] The essence of preparing high quality polymer-clay nanocomposites is to achieve nano-dispersion of clay into polymer matrix. In general, two types of nanomorphologies of clay can be prepared (as shown in figure 15), namely, intercalated and delaminated (or exfoliated). \[28\]

![Figure 15 Schmeatic showing polymer-clay nanocomposite. (courtesy of J.H. Koo)](image_url)

Intercalated morphologies are achieved by self-assembled, well-ordered multilayered
structures. Between gallery spaces (2-3nm) of those parallel individual silicate layers, the extended polymer chains are inserted. And when the spaces between individual silicates are large enough that the interactions between gallery cations of the adjacent layers are no longer existed, the delaminated nanocomposites are obtained. In this case, the interlayer spacing can be of the order of the radius of gyration of polymer and the clay additives are considered as well dispersed in polymer. [39] Nanoclay can be inorganic and organic in nature. Inorganic clays are acquired naturally while the types of organic clays can be diversely depending on their post treatment. More detailed information will be introduced in chapter 4.

During the past few decades, tremendous results were obtained regarding to the fire performance of polymer-clay nanocomposites. J. Zhu et al found that when only 0.1% mass fraction of clay was incorporated into polystyrene, the PHRR rate was reduced by more than 40% and the onset degradation temperature was also increased by 40°C when compare to the pristine polymer. [40] The fire behavior of polystyrene polymer mixed with silicon-methoxide-modified clays was also studied by the same research group. They pointed that also methoxide might react with clay hydroxyl group to link the cation and the clay together, the nanocomposites did not show any difference in terms of flammability when compared with other polystyrene nanocomposites. [41] J.W. Gilman et al compared the effectiveness of different kinds of layered silicates when they were added into polystyrene. In their research, they found that fluorohectorite had no effect on PHRR whereas montmorillonite showed 60% decreasing in PHRR. The study claimed that the
nanodispersion, types of layered silicate and processing conditions would influence the fire behavior of nanocomposites. [42] Furthermore, studies carried out by Morgan et al indicated that some other factors including the clay loading and polymer melt viscosity would also affect the flammability of polystyrene-clay nanocomposites.[43-44] Many other polymer-clay nanocomposites with different matrices such as polypropylene, [45] polyethylene, [46] PMMA, [47] PVC, [48-50] EVA, [51-52] polyamide-6, [53] vinyl ester,[54] unsaturated polyester, phenolic resins [55] etc were also found great improvement in fire performance in terms of PHRR and TGA. All these studies indicated that the intrinsic properties of parent matrix would influence the effectiveness of nanoscale additives that aimed to enhance the fire performance of composites. Different mechanisms should be introduced to explain those phenomena. Gilman suggested that the clay may change the decomposition products depending on the polymer matrix; it may cause cross-linking and ultimately catalyze carbonaceous char formation. [38]

Some other researchers had reported that a graphite-type char formed during the combustion of polymer-clay nanocomposites, indicating that polymer-graphite nanocomposites might have the potential to become flame resistant materials. [53] Actually, expanded graphite and graphite oxide which been considered as another type of nanoparticles that had layered structure had already been studied as fire retardants for years. M.R. Nyden et al conducted molecular dynamic simulations of the thermal degradation of nano-confined polypropylene. The thermal degradation was performed as a function of the gallery spaces
between individual graphite sheets. The mass loss of polymer-clay nanocomposites results indicated that when the space was 3.0nm, there was a pronounced improvement of thermal stability of the nanocomposites which resulted from interaction between polymer molecular and polymer molecular with graphite. However, when the distance of gallery space was less than 2.5nm, the density of polymer in the narrow space between the graphite sheets was very high which made the polymer relatively unstable due to the van der Waals repulsions between atoms. Nevertheless, when the space between graphite was too larger, the degradation products tended to escape from the spaces between the sheets easily, which is different to mechanical applications where large gallery space was preferred. [56] Motivated by their study, Uhl et al studied the fire resistant effect of graphite when incorporated into polystyrene. Two approaches were used for preparing nanocomposites: in situ polymerization and melt blending. Organically modified and as received graphite oxide where used. The loading of modified graphite oxide were varied from 1% to 5%. The XRD results showed that the exfoliated structures were obtained when 1% of modified graphite oxide was mixed into polymer. And intercalated structures were achieved when higher loading of modified additives were incorporated. Moreover, polymer with modified graphite oxide had a d-spacing much larger than the intercalated structures that formed used nonmodified graphite oxide. They observed that the PHRR were reduced by 27-54% depending on the loading of modified graphite oxide i.e. higher loading graphite oxide had higher reduction. Similar results were obtained in melt blending approach. The only difference was that the latter
approach led to a narrower d-spacing between graphite sheets compare with in situ polymerization method. [57-58] When compared PS-graphite nanocomposites to the PS-clay nanocomposites with 3 and 5% clay content, the PHRR reduction of in situ polymerized PS-graphite system was roughly 50% value of the latter samples. [59] However, there was no significant increasing in terms of thermal stability for all samples in their research.

Xu, Yasmin et al reported more pronounced improvement in thermal stability when graphite was introduced in poly (vinyl alcohol) and epoxy system. [60-61] The fire performance of phenolic-graphite and epoxy-graphite systems was studied and compared to composites with fiberglass and aramid as filler. The results showed that phenolic-graphite system had the best flame resistance whereas the epoxy-graphite composite had worst flame resistance. [62] However, it was not clear whether the graphite particles were dispersed in nanoscale, since the dispersion had significant effect on fire performance of parent polymer. By using emulsion polymerization technique, the effective of graphite oxide on the flame resistance of styrene-butyl acrylate copolymer and polystyrene was studied by R. Zhang et al. They found that there was a drastic reduction in PHRR. [63-65] However, it was suggested that due to the thermal degradation of its organic emulsifier, the time to ignition was shorter than the pristine sample. [66] Moreover, Kashiwagi et al claimed that due to the difference of transmission property between pure polymer and polymer mixed with carbon based nanofiller, the time to ignition would be shorter for the latter samples. [67] Uhl et al examined the flame resistance property of polyamide-graphite and polystyrene-graphite nanocomposites, the
reduction in PHRR were achieved at a level that similar to the clay polymer systems. [68-69]

Other types of very famous carbon based nanofillers are single walled nanotubes (SWNT), multi walled nanotubes (MWNT) and carbon nanofibers (CNF). Carbon nanotube (CNT), more specifically MWNT is first synthesized in 1991 by Iijima. [70] Later in 1993, Bethune et al discovered SWNT. [71] Since then various types of advanced materials that exhibit splendid properties were invented, leading the nanotechnology development into a new era. CNT essentially can be considered as rolling up a graphene sheet into a cylindrical structure as shown in figure 16. [72]

![Figure 16 Rolling up a graphene sheet to form a nanotubes. (courtesy of C.M. Lieber)](image)

It is necessary to stress that when the orientation of rolling up a graphene is different, various types of CNT would be obtained as shown in figure 17. The diameter of CNT can range from 0.3 nm to around 10 nm with aspect ratios of $10^5$-$10^6$. 

39
While one layer of graphene sheet will form SWNT, MWNT can be obtained by rolling up multiple layers of graphene sheets. In general, the gallery distance between layers is about 0.36 nm as shown in figure 18.

The researches about CNT are abundant, reporting CNT possesses exceptionally high elastic properties, large elastic strain, fracture strain sustaining capability, special electrical conductivity properties and high thermal conductivity. [73-76] For example, the elastic modulus of a SWNT is about 1 TPa and its density is only around 1.2 g/cm³ while iron
typically has an E of 200Gpa and $\rho$ of 7.8g/cm$^3$.

Although CNF has a cylindrical nanostructure, unlike CNT, the arrangement of graphene layers of CNF can be varied diversely as shown in figure 19. The average diameter of CNF is larger than CNT which is about 70-200nm. And its length is about 50-100μm. The mechanical properties of CNF in general are at a lower grade than that of CNT. However, the price of CNF is far more attractive. Furthermore, CNF is welcomed by its scale-up capability.

[77]

![Figure 19 Schematic renditions of various of types of CNF.](freepatentsonline.com)

The flammability of composites that mixed with those two-dimensional carbon based nanoscale fillers had been studied by Kashiwagi et al intensively. Besides cone calorimeter in air, they also examined the flammability of nanocomposites with gasification device in a nitrogen atmosphere. One advantage of gasification device as shown in figure 20 is that it allows researchers to take video record of the gasification process which help them to appreciate the mechanisms of flame resistant of CNF/CNT based nanocomposites in a vivid manner. [78]
For completeness, Kashiwagi et al also studied the effect of other tubular nanoparticles i.e. alumina silicate nanotube (ASNT) and non-tubular carbon based particles i.e. carbon black. During their years of research, they found out that there were five factors related to the fire performance of those nanocomposites, namely, the type and concentration of nanotubes, the dispersion of nanotubes in polymers, molecular weight of resin, viscoelastic characteristics of nanocomposites, and finally the aspect ratio of nanoparticles (length divided by outer diameter of tubes). Kashiwagi et al reported that well dispersed SWNTs showed best effectiveness to reduce the flammability of PMMA. For example, only 0.5 wt% of SWNT in the PMMA nanocomposites exhibited more than 50% reduction in PHRR compared to neat PMMA. However, when the mass fraction of SWNTs was less than 2%, the flame retardancy of the nanocomposites was poor. Moreover, the poorly dispersed SWNTs in polymer leaded to higher PHRR than those SWNTs were well-dispersed. Kashiwagi et al explained that a well dispersed SWNTs sample would form a char layer that had continuous compact network structure. The char layer act as protective layer which resisted both heat convection and radiation as well as slowed down mass (fuel) flow. Additionally, they studied the rheological behavior of nanocomposites. They pointed out that the greatest increasing in viscosity of PMMA occurred when adding 0.5wt% of SWNT which resulted in a solid-like behavior of nanocomposites during combustion process. This phenomenon ultimately leaded to a formation of the high quality char layer. Furthermore, they suggested that the integrity of the network at high temperatures can be expected to be influenced by the molecular mass of the
polymer matrix.

In order to address the effect of aspect ratio of CNTs on flammability property of nanocomposites, Kashiwagi et al studied two different MWNTs with aspect ratios of 49 and 150 respectively. The results indicated that the aspect ratios did not influenced thermal stability of nanocomposites. However, MWNTs had large aspect ratios tended to increase the complex viscosity and storage modulus of parent polymer matrix. As a result, nanocomposites that contained large aspect ratios of MWNTs significantly reduced the flammability of polymers. [67][79-83]

Besides those nanoparticles have linear and planar structure, the three dimensional nanoscaled particles are also studied by researchers very recently by the virtue of the discovery and development polyhedral oligomeric silsesquioxane (POSS). [67] As shown in figure 21, a POSS is composed by inorganic silica like core and organic functional groups...
that attached to its 8 corners. POSS particles exhibit excellent oxidation stability due to its intermediate structure between silicone and silica and compatibility to polymer because of its organic groups. The three dimensional nanoscaled structures enable their large interface area with host polymer. As a consequence, the viscosity might be improved which is extremely desirable to enhance the quality of char during combustion as mentioned in the proceeding paragraphs. With these characteristics, POSS particles are demonstrated as effective flame retardants by the facts of improvement in thermal stability and flame resistance of their host polymers. \[84\][85] If POSS particles contained function groups that do not readily undergo cross-linking reactions, then they would only evaporated at high temperatures. During combustion, instead of evaporating directly, they initially decompose by partial loss of their organic groups which have no significant effect on the degradation of the parent polymers, following by cross-linking reaction with polymer which incorporates the polymer into the SiO$_x$C$_y$ networks i.e. char.\[86\][87] The types of POSS particles are various depending on their organic substituents. More detailed introduce would be carried out in the next chapter.

Figure 21 A general schema of POSS. (matdl.org)

Yong Ni et al found that when increasing the loading of POSS in polymer, the thermal
stability and residue yield of the polymer matrix increased when conducting thermal gravimetric analysis.[86] [88-89] Gupta et al studied the flame resistant property of epoxy vinyl ester resin containing POSS. The results showed that a reduced heat release rate and smoke. Furthermore, unlike carbon base nanofiller, the ignition time of the nanocomposites was delayed. Therefore, they claimed that the mechanism of POSS to retard flame was the reduction fuel volatilization, the formation of stable and non-permeable surface chars. [90] Devaux et al found a simultaneous reduction in total heat release and heat release rate when 10% mass fraction of POSS particles were introduced into polyurethane (PU) which was coated onto PET knitted fabric. They explained that the reduction in flammability should be contributed to the high thermal stability of the nanocomposites and formation of uniform and compact char residue during combustion reaction. [91] Okoshi and Nishizawa also reported the high quality char formed when POSS based nanocomposites were coated onto the surface of polycarbonate. [92] However, the flame resistant efficiency of POSS based nanocomposites as a whole have not been extensively studied because of their high cost and sometimes failing to form strong residue when compared to clay or nanotubes based nanocomposites.[93] Kashiwagi et al studied the flame retardancy of POSS in PTME-PA, SBS and PP. They found that even though the PHRR was decreased, the total heat release of the nanocomposites didn’t show significant reduction. Moreover, the char analysis indicated that when POSS particles were incorporated into polymer, there was no great increase in carbonaceous char yielding and the majority of residue composed by the inorganic
component of the POSS. [94] Another study examined the flammability of POSS in textiles. They found that there was no effect on PHRR even though the time to ignition was delayed, indicating that POSS only served as a thermal stabilizer rather than flame retardant. [94] Moreover, a recent study showed that when trisilanol phenyl POSS particles were incorporated into PMMA, no significant flammability reduction was observed during cone calorimeter test. [96] General speaking, the flammability of nanocomposites containing POSS depends on three factors, namely, the structure of POSS particles, the type of polymer matrix and the dispersion and/or incorporation of POSS into the polymer structure. As long as a certain type of POSS could increase their cross-links with parent polymer and form large amount of SiO$_x$C$_y$ network, the flame retardancy of the nanocomposites would be improved in terms of reduction in both PHRR and total heat release. [67].
CHAPTER 3
MORPHOLOGY, THERMAL STABILITY, AND FLAMMABILITY OF FRPC COATED WITH HYBRID NANOPAPERS

3.1. Introduction

POSS is such a type of material that represents a merger between chemical and filler technologies which involves a concept of incorporating inorganic blocks into organic polymers. Hybrid Plastics has launched more than 250 different types of POSS particles by the modification of their organic substituents, making them become important molecular level reinforcement, multifunctional polymer additives, processing aids and flame retardants. (figure 22)

![Figure 22 Unique properties of POSS. (courtesy of Hybrid Plastics)](image)

As mentioned in the last chapter, POSS is composed by inorganic silica like core and organic functional groups. The chemical structure is schematically showed in figure 23. This unique structure makes POSS exhibits remarkable chemical stability and compatibility to
polymer matrix. [67] Furthermore, the viscosity of polymer is expected been increased when the nanosized POSS is incorporated. As a consequence, the quality of char formed during combustion reaction would be improved thus a reduction in flammability. Indeed many studies report the reduction in flammability of POSS nanocomposites while others suggest that the improved flame resistance is limited. [84-96] Since a char layer that is defined as effective not only show low thermal conductivity which protect underlying structure from degradation but also should have low permeability which prevent immigration of fuel and oxygen, the poor effect on flammability of POSS based nanocomposites might be attribute to the relatively high permeability of char due to the cage like structure of POSS.

Figure 23 Chemical structure of POSS. (from Morgan and Wilkie [2007])

In this chapter, the hybrid nanopapers combining POSS with CNFs are fabricated. The hybrid nanopapers are then coated on the surface of glass fiber reinforced polymer matrix composites through RTM process. The morphology, thermal stability, and flammability of the nanopapers and nanocomposites are studied. The flame retardant mechanism of hybrid
nanopapers in composite laminates is also discussed. In addition, a preliminary study of fire performance related characteristics of clay-CNFs hybrid is introduced.

3.2. Experiment Method

3.2.1. Materials

Vapor grown carbon nanofibers (Polygraf III PR25-PS) are supplied by Applied Sciences, Inc. with a diameter of 50-100nm and a length of 30–100 μm. The Cloisite Na⁺ clay is obtained from Southern Clay, Inc. and OctaVinyl POSS (OL1160) is supplied from Hybrid Plastics, Inc. The glass fiber (GF) is supplied from Composites One, Inc. with a surface density of 800 g/m². The unsaturated polyester resin (product code: 712–6117, Eastman Chemical Company) is used as matrix material for laminated composites with the MEK peroxide as hardener at a weight ratio of 100:1.

3.2.2. Processing of hybrid nanopapers and nanocomposites

The as-received CNF powder was dispersed in distilled water with an aid of surfactant Triton-X100. The mixture was then sonicated using a high intensity sonicator (600-watt Sonicator 3000 from Misonix Inc.) for 30 min with a power of 30-50 watts. The solution was subsequently filtered under a high-pressure compressed air system to fabricate the nanopaper. The as-prepared nanopaper was dried in an oven at 120 ℃ for 2 h. In this study, two types of hybrid nanopapers, which combined CNFs with POSS or clay, were fabricated with different
weight ratios as shown in table 6.

Table 6 Composition of CNF-POSS and CNF-clay hybrid nanopapers and their nanocomposites.

<table>
<thead>
<tr>
<th>Nanocomposite sample ID</th>
<th>Contents (wt %)</th>
<th>Weight ratios in the nanopaper</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GF</td>
<td>Resin</td>
</tr>
<tr>
<td>CNF-POSS-1 laminates</td>
<td>52.73</td>
<td>45.65</td>
</tr>
<tr>
<td>CNF-POSS-2 laminates</td>
<td>51.89</td>
<td>45.36</td>
</tr>
<tr>
<td>CNF-POSS-3 laminates</td>
<td>51.96</td>
<td>43.76</td>
</tr>
<tr>
<td>CNF-POSS-4 laminates</td>
<td>50.58</td>
<td>36.20</td>
</tr>
<tr>
<td>CNF-Clay-1 laminates</td>
<td>53.22</td>
<td>45.68</td>
</tr>
</tbody>
</table>

Resin transfer molding (RTM) process was used to fabricate laminated composites which eight layers of glass fiber mats were used as reinforcement. Before the RTM process, one layer of CNF-POSS or CNF-clay hybrid paper was placed on the bottom of an aluminum mold. The unsaturated polyester resin was then injected into the mold under an 80 psi pressure. After resin was cured at room temperature for overnight, the composite panels were further post-cured at 120 °C for 2 h. The weight ratios of resin, glass fiber and nanopaper of these samples were showed in table 6.

3.2.3. Characterization and evaluation

- Scanning Electron Microscopy

  The hybrid nanopapers and the nanopapers infused with the polyester resin were sputter-coated with a conductive gold layer for SEM analysis. The SEM images were obtained by a Zeiss Ultra-55 at 5 kV which equipped with an energy dispersion analysis of X-ray (EDAX).
Thermogravimetry-Fourier Transform Infrared Spectra (TGA-FTIR)

The TGA-FTIR instrument consisted an analyzer (TGA-Q5000, TA Co., USA) coupled with a Fourier transform spectrometer (Nicolet 6700) and the transfer line. The characterization was conducted under nitrogen atmosphere at a flow rate of 35.0 ml/min for TG with a heating rate of 20 °C/min. It was important to note that during the combustion reaction, almost all the oxygen was consumed by reacting with the gas phase fuel, ideally no oxygen should participate the degradation process occurred in the liquid phase. Therefore, rather than air, the nitrogen atmosphere was preferred for the TGA analysis where the actual condition was more precisely simulated. Furthermore, in order to reduce the possibility that gas might condense along the transfer line, the temperature in the gas cell and transfer line was set to 230 °C. The dynamic FTIR spectra were obtained in-situ during the thermal degradation of test samples.

Con Calorimeter Tests

The fire retardant performance of composite laminates coated with the hybrid nanopaper was evaluated with cone test at an incident heat flux of 50 kW/m² in accordance with ASTM E1354/ISO 5660. Each set of test samples had a thickness of 7.3±0.1 mm and were cut into circular disks with a diameter of 75±0.1 mm using a water jet. These samples were wrapped in an aluminum foil before cone tests. All the cone tests were conducted with the samples in horizontal position. And the surface coated with hybrid nanopaper was directly exposed to the external heat radiation.
3.3. Results and Discussions

3.3.1. Morphologies of nanopapers and nanopapers infused with polyester resin

The morphologies of hybrid nanopapers are showed in figure 24. It can be seen that CNFs are uniformly dispersed and highly entangled with each other. At the bottom surface of the CNF-POSS nanopaper, CNFs are more compact compared than those at the top surface. This is due to the deposition of POSS particles during the high pressure filtration process. The POSS particles cannot be observed directly in the nanopapers where the weight ratios of CNF/POSS are 9/1 and 1/1. However, the EDAX results confirm the existence of POSS particles in the nanopapers as shown in figure 25. When the weight percentage of POSS within hybrid nanopapers is increased to 70 wt%, the POSS particles then can be observed at the bottom surface of the nanopaper. And the EDAX indicates that the silicon content is increased dramatically as shown in figure 25c. In the nanopapers where the CNF/POSS weight ratio is decreased to 1/9, the POSS particles can be observed even at the top surface as shown in figure 24g. And the large POSS aggregates are found on the bottom surface (see figure 24h.). As a result, the EDAX shows the intensity of silicon is much higher than carbon as shown in figure 25d.
Figure 24 SEM images of hybrid nanopapers: (a) top surface of CNF-POSS-1 nanopaper; (b) bottom surface of CNF-POSS-1 nanopaper; (c) top surface of CNF-POSS-2 nanopaper; (d) bottom surface of CNF-POSS-3 nanopaper; (e) top surface of CNF-POSS-3 nanopaper; (f) bottom surface of CNF-POSS-3 nanopaper; (g) top surface of CNF-POSS-4 nanopaper; (h) bottom surface of CNF-POSS-4 nanopaper; (i) top surface of CNF-clay-1 nanopaper; and (j) bottom surface of CNF-clay-1 nanopaper.
Figure 25 EDX on the bottom surface of hybrid nanopapers: (a) CNF-POSS-1 nanopaper; (b) CNF-POSS-2 nanopaper; (c) CNF-POSS-3 nanopaper; (d) CNF-POSS-4 nanopaper; and (e) CNF-Clay-1 nanopaper.

As shown in figure 24i and figure 24j, for the CNF-clay nanopapers, clay particles cannot be observed on the top surface. However, the SEM image indicates that clay platelets and CNFs are homogeneously dispersed and entangled with each other on the bottom surface of the nanopaper. It is necessary to stress that it takes much more time to filter out the water in CNF-clay suspension than that of the CNF-POSS suspension during paper-making process which indicates the permeability of the CNF-clay nanopaper is much lower than the CNF-POSS nanopaper.

Figure 26 shows the morphologies of hybrid nanopapers infused with the polyester resin. It is clearly showed that CNFs are still homogenously dispersed. The polyester resin fully fills up the pores within the nanopapers. The POSS particles cannot be identified in the SEM images probably due to the vinyl groups on the POSS particles (initiated by curing argent) are cross-linked with the polyester resin.
Figure 26 SEM images of hybrid nanopapers infused with the polyester resin: (a) CNF-POSS-1; (b) CNF-POSS-2 nanopaper with resin; (c) CNF-POSS-3 nanopaper with resin; and (d) CNF-POSS-4 nanopaper with resin.

3.3.2. Thermal stability of nanopapers and nanopapers infused with polyester resin

The thermal stability of hybrid nanopapers is related to the fire performance of composites. TGA is one of the most widely used techniques to evaluate the thermal stability of various types of materials. The TGA results of the pristine CNF, POSS, and polyester resin are shown in figure 27. The decomposition of the pristine POSS occurs in the range of 210 - 220 °C with about 2 wt% residue at 600 °C as shown in table 7 and figure 27. The polyester resin begins to
decompose at about 274 °C and the residue is about 5.5 wt% at 600 °C. The weight loss of CNFs at 600 °C is about 1.5 wt% indicating that the thermal stability of CNFs been used in this study is extremely high.

Table 7 Thermal properties of particles, nanopapers and nanocomposites from TGA.

<table>
<thead>
<tr>
<th>TGA Test Samples</th>
<th>T-5wt% (°C)*</th>
<th>Char (wt%)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>POSS</td>
<td>213.2</td>
<td>2.05</td>
</tr>
<tr>
<td>Resin</td>
<td>273.6</td>
<td>5.52</td>
</tr>
<tr>
<td>CNF</td>
<td>/</td>
<td>98.5</td>
</tr>
<tr>
<td>Clay</td>
<td>/</td>
<td>97.5</td>
</tr>
<tr>
<td>CNF-Clay-1 nanopaper</td>
<td>/</td>
<td>95.8</td>
</tr>
<tr>
<td>CNF-POSS-1 nanopaper</td>
<td>199.0</td>
<td>92.3</td>
</tr>
<tr>
<td>CNF-POSS-1 nanopaper with resin**</td>
<td>285.6</td>
<td>19.6</td>
</tr>
<tr>
<td>CNF-POSS-2 nanopaper</td>
<td>190.1</td>
<td>64.6</td>
</tr>
<tr>
<td>CNF-POSS-2 nanopaper with resin**</td>
<td>257.2</td>
<td>19.3</td>
</tr>
<tr>
<td>CNF-POSS-3 nanopaper</td>
<td>210.1</td>
<td>33.0</td>
</tr>
<tr>
<td>CNF-POSS-3 nanopaper with resin**</td>
<td>231.1</td>
<td>34.7</td>
</tr>
<tr>
<td>CNF-POSS-4 nanopaper</td>
<td>206.5</td>
<td>15.2</td>
</tr>
<tr>
<td>CNF-POSS-4 nanopaper with resin**</td>
<td>222.1</td>
<td>16.4</td>
</tr>
</tbody>
</table>

*Temperature at 5 wt% weight loss; ** there is no glass fiber in these samples.
The thermal properties of hybrid nanopapers are shown in figure 28 and table 7. The decomposition of the CNF-POSS nanopaper occurs in the range of 190-206 °C as listed in table 7. The residue decreases with increase the loading of POSS in the nanopapers. When the weight percentage of POSS increases from 10% (CNF-POSS-1 nanopaper) to 90% (CNF-POSS-4 nanopaper), the residue decreases approximately from 96 wt% to 15 wt%. For the nanopapers infused with polyester resin, the decomposition temperature increases significantly which occurs in the range of 222-285 °C. The increase of degradation temperature is due to the higher thermal stability of the polyester resin as indicated in figure 27. During the curing of resin, the POSS particles could cross-link with the unsaturated polyester molecules. It is interesting to note that when the weight percentage of POSS in the nanopaper is more that 70 wt% (CNF-POSS-3 nanopaper with resin), the residue is more than that of the nanopaper without the resin as shown in table 7. Similar results of residue are obtained for CNF-POSS-4 nanopaper with resin (90 wt% of POSS). This is probably caused by the increase of cross-link density between POSS particles and unsaturated polyester resin molecules. Figure 28(e) is the
TGA results of the pristine clay and CNF-clay nanopaper. Their weight loss at 600 °C is about 2.5 wt% and 4.2 wt%, respectively. This reveals that clay and the CNF-clay nanopapers are more stable than POSS and the CNF-POSS nanopapers.
3.3.3. Real-time FTIR of hybrid nanopapers and nanopapers infused with resin

The changes in chemical structures of hybrid nanopapers with and without polyester resin during thermal degradation are monitored by real-time FTIR. The TGA-FTIR technique can directly give an identification of volatilized products to help understand thermal degradation mechanism. In this study, the characterization of the volatilized products by TGA-FTIR instrument is conducted in nitrogen atmosphere. The 3D FTIR spectrums of the evolved gases of hybrid nanopapers with and without resin at different time are shown in figure 29. The FTIR spectra of hybrid nanopapers without resin (CNF-POSS-1 nanopaper and CNF-POSS-4 nanopaper) are shown in figure 29(a) and 29(b). The peaks in the regions of around 3400-4000 cm\(^{-1}\), 2250-2400 cm\(^{-1}\), 2700-3000 cm\(^{-1}\), and 1110 cm\(^{-1}\) are observed. For the nanopapers
infused with the resin (figure 29 c and d), the peaks in the regions of around 3400-4000 cm⁻¹, 2700-3070 cm⁻¹, 2250-2400 cm⁻¹, 1400-1867 cm⁻¹, 907-1262 cm⁻¹ are observed. The spectra fit well to the reported FTIR features of gas products such as H₂O (3400-4000 cm⁻¹), aromatic C-H (3060 cm⁻¹, stretching vibration), hydrocarbons (2800-3000 cm⁻¹), CO₂ (2250-2400 cm⁻¹), carbonyl compounds (1400-1867 cm⁻¹), ester C-O-C (1260 - 1000 cm⁻¹, asymmetric and symmetric stretching vibrations) and Si-O (stretching vibration at 1110 cm⁻¹). [97-99]

Figure 29 3D FTIR spectra of evolved gases produced by the pyrolysis of CNF-POSS nanopaper with and without resin: (a) CNF-POSS-1 nanopaper; (b) CNF-POSS-4 nanopaper; (c) CNF-POSS-1 nanopaper with resin; and (d) CNF-POSS-4 nanopaper with resin.

The characteristic spectra of the selected nanopapers (without resin) at different temperature
(from 240-600 °C) are shown in figure 30 (a) and (b). Here CNF-POSS-1 and -4 nanopapers are selected for their vast difference in the ratio of CNF/POSS. Some small molecular gaseous products such as CO₂ and H₂O are easily identified by their characteristic absorbance (CO₂ at 2357 cm⁻¹, and H₂O at 3400-4000 cm⁻¹). [97] The alkyl and carbonyl compounds are observed at around 2980 cm⁻¹ and 1740 cm⁻¹ from 320-560 °C, respectively. The aromatic C-H is also observed at around 3060 cm⁻¹, which is probably due to the decomposition of POSS particles. Figure 30 (b) shows that the -Si-O- peak is detected at about 200 °C in the CNF-POSS-4 nanopaper, and the -Si-O- absorption band is detected at about 320 °C in the CNF-POSS-1 nanopaper. The nanopapers are varied from the CNF-dominated structure to the POSS-dominated structure, depending on their weight ratios (CNF/POSS = 9/1 to 1/9). During the TGA test, POSS particles are relatively easy to migrate and sublimate, [100] and therefore the IR detects the -Si-O- absorption earlier and at lower temperature in the nanopaper with CNF/POSS = 1/9. The intensity of -Si-O- increases when the temperature is increased to more than 400 °C, where 98% weight loss of POSS is observed in figure 27.
Figure 30 FTIR spectra of volatilized products at different temperature during thermal degradation: (a) CNF-POSS-1 nanopaper; (b) CNF-POSS-4 nanopaper; (c) CNF-POSS-1 nanopaper with resin; and (d) CNF-POSS-4 nanopaper with resin.

The FTIR spectra of pyrolyzed products of CNF-POSS-1 and -4 nanopapers with resin are showed in figure 30 (c) and (d). The most important absorption bands in the IR spectrum of such nanocomposites are associated with -Si-O- (1110 cm⁻¹, stretching vibration), carbonyl compounds C=O (1744 cm⁻¹, stretching vibration), ester C-O-O (1262 and 1002 cm⁻¹, asymmetric and symmetric stretching vibrations), vinyl C=C (910 cm⁻¹ stretching vibration), aliphatic C-H (2950-2800 cm⁻¹, asymmetric and symmetric stretching vibration), carboxylic groups (3000-2600 cm⁻¹), aromatic C-H (3069 cm⁻¹, stretching vibration) and CO₂ at 2367 cm⁻¹.

[97-99] The early volatilized products at 300 °C are identified as CO₂, -Si-O-, aliphatic and carbonyl moieties, which could come from the decomposition of functional groups of POSS and the scission of the polyester resin. It is interesting to note that in the CNF-POSS-4 nanopaper with resin sample, the aromatic C-H exhibits a strong absorption at 3069 cm⁻¹ at 300 °C. However, in the sample of CNF-POSS-1 nanopaper with resin, this peak cannot be
observed. The intensity of the above pyrolyzed products from the former sample is much more than those from the latter one. The difference in the intensity of pyrolyzed products indicates that the formation of char materials in the former sample is earlier and at a lower temperature than latter sample. When the temperature is increased to 360 °C, the new ester C-O-C (1263 cm⁻¹) and vinyl C=C (910 cm⁻¹) absorption band caused by the decomposition of the polyester resin are observed in both nanocomposites. This decomposition process is likely to be completed at 500 °C, leading to the decrease in the intensity of C-O-C and CH₂=C- absorption bands. Based on the combined results of TGA and IR study, one can conclude that POSS particles decomposes at early stage, generating volatilized aliphatic and -Si-O- moieties, following by the decomposition of polyester resin, resulting in the volatilization of aromatic and carbonyl moieties, and vinyl compound.

3.3.4. Cone calorimeter tests of composite laminates coated with hybrid nanopapers

The cone calorimetric results for the control sample and various composite laminates coated with hybrid nanopapers are shown in table 8 and figure 31. After the ignition, the heat release rate increases rapidly to maximum values and then decreases gradually. The peak heat release rate (PHRR) of the control sample (without nanopaper on the surface) is 375.9 kW/m² as shown in figure 31 (a) and (b). For composite laminates coated with the CNF-POSS nanopapers, the PHRR increases dramatically. The PHRR reaches up to 755.93 kW/m² when the weight percentage of POSS is 50wt% in the nanopaper. And the PHRR decreases with the
increase of the POSS loading in hybrid papers. The PHRR drops to 367.2 kW/m² with 90 wt% of POSS particles are presented in the nanopaper. For the laminates coated with CNF-clay nanopapers, the PHRR is 125.2 kW/m², a reduction of 67% when compared to the PHRR of the control sample. However, the time to ignition is longer than control sample as shown in figure 31 (c) and (d).

Table 8 Cone calorimeter data for the nanocomposites coated with hybrid nanopaper.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PHRR (KW/M²)</th>
<th>THR* (MJ/m²)</th>
<th>ASEA* (m²/kg)</th>
<th>AMLR* (g/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control sample</td>
<td>375.9±34.6</td>
<td>134.0±8.2</td>
<td>1044.1±60.0</td>
<td>0.034</td>
</tr>
<tr>
<td>CNF-POSS-1 laminates</td>
<td>557.4±25.0</td>
<td>135.3±5.2</td>
<td>898.6±10.5</td>
<td>0.028</td>
</tr>
<tr>
<td>CNF-POSS-2 laminates</td>
<td>755.9±64.2</td>
<td>143.5±10.4</td>
<td>926.2±46.3</td>
<td>0.027</td>
</tr>
<tr>
<td>CNF-POSS-3 laminates</td>
<td>608.5±5.4</td>
<td>162.5±22.5</td>
<td>889.5±53.5</td>
<td>0.028</td>
</tr>
<tr>
<td>CNF-POSS-4 laminates</td>
<td>367.2±53.2</td>
<td>145.1±2.2</td>
<td>775.2±1.5</td>
<td>0.034</td>
</tr>
<tr>
<td>CNF-Clay-1 laminates</td>
<td>125.3±2.1</td>
<td>63.5±3.0</td>
<td>673.2±61.6</td>
<td>0.025</td>
</tr>
</tbody>
</table>

* THR: total heat release; ASEA: average specific extinction area; AMLR: average mass loss rate.
POSS is a candidate material for flame retardant nanocomposites and the PHRR of polymer mixed with POSS particles is decreased significantly compared to the virgin polymer. [101] In this study, the PHRR increases when POSS particles are incorporated into the nanopaper. Since CNFs are concentrated on the top surface of nanocomposites, the absorbance of radiation from external heat flux will be higher. However, the heat conduction in the thickness direction of composite laminates is slow due to the low thermal conductivity of glass fiber. Therefore, the heat absorption will cause a rapid increase of the surface temperature. The POSS particles are embedded in the CNF networking structure and are heated by the concentrated heat caused by CNFs. Yet, the thermal stability of POSS is low. As a consequence, flammable products come from the decomposition of functional groups of POSS particles would lead to an early ignition of composite laminates coated with the CNF-POSS nanopapers. In addition, as discussed in previous paragraphs, POSS particles tend to migrate to the surface of polymer nanocomposites and sublime even at 96 °C which ultimately will increase the HRR of the samples.
The CNF-clay nanopaper has better fire retardant performance than the CNF-POSS nanopaper. The thermal stability of clay is much higher than both POSS particles and polymer resin, as shown in table 7 and figure 27. The flammable volatilizations come from the decomposition of the resin instead of clay. Clay has a layered structure, serving as barrier for mass immigration and heat transfer. In the CNF-clay nanopaper, the clay layers will attenuate the concentration of the heat absorbed by CNFs from the external heat flux. The time to heat up the fuel to the ignition point will be extended. Furthermore, the CNF networks and the clay layers in the nanopaper are reinforced with each other, which provide a low permeability and therefore limit the diffusion of O$_2$ to the substrate and of the volatilized gas to the surface to feed the flame. However, POSS has a cage-like structure with organic groups attaching to the eight corners of the cage. There is no barrier effect for such a cage-like structure.

3.3.5. Morphologies of char materials after cone calorimeter tests

The analysis of char materials after cone test can provide an insight into flame retardant mechanism. Figure 32 shows the morphologies of the residue of composite laminates coated with hybrid nanopapers. It can be seen that the morphologies of the char vary in appearance, shape, and the extent of compaction. In figure 32 (a), only CNFs and a few floccules are observed, which is probably due to the pyrolysis of POSS particles and the polyester resin. In figure 32 (b), CNFs are much shorter and more floccules can be found. In addition, small cracks are found on the surface. As shown in figure 32 (c), a significant increment of the
quantity of cracks is observed within the hybrid nanopaper where the weight percentage of POSS particles is 70 wt%. The quality of the char corresponds to the fire retardant performance of composite laminates. As a result, during cone calorimeter tests, these composite samples exhibit much higher PHRR.

For the samples containing 90 wt% POSS particles, the char exhibits different morphology as shown in figure 32 (d). There is no floccule on the surface. The entire surface is covered by a ceramic-like sintered layer, and nearly no CNF or cracks can be found. This char layer could serve as an effective barrier, limiting the heat immigration and mass transfer rates, thus slowing down the combustion and degradation of the polymer resin. Figure 32 (e) shows the morphology of the char for composite laminates coated with the CNF-clay nanopaper. It can be seen that the clay particles and CNF networks are reinforce with each other and form a compact protective layer. This layer could effectively limit the transmission of the heat and the supply of the flammable fuel, resulting in a dramatic decrease in the PHRR.
Figure 32 SEM of char materials of composite laminates coated with hybrid nanopapers after cone test: (a) CNF-POSS-1 laminates; (b) CNF-POSS-2 laminates; (c) CNF-POSS-3 laminates; (d) CNF-POSS-4 laminates; (e) CNF-clay-1 laminates.

3.4. Conclusions

In this study, the CNF-POSS and CNF-clay nanopapers are developed and coated onto the surface of composite laminates through RTM process. The SEM images show that CNFs are dispersed homogeneously in the hybrid nanopapers. And POSS particles tend to aggregate at a high content of 90 wt%. The SEM-EDAX verified the increase in Si intensity with the content of POSS particles increased in the nanopaper. In the CNF-clay nanopaper, the clay platelets
and CNFs are tangled with each other, resulting in a low permeability nanopaper. The TGA test results show that the addition of POSS particles in hybrid nanopapers will decrease their thermal stability. The real time TGA-FTIR test indicates that the Si moiety is produced at a low temperature. The main products of the thermal decomposition of the nanopaper infused with the polyester resin are CO₂, H₂O, aromatic, vinyl, hydrocarbons moieties, etc. It is found that the heat release rates of composite laminates coated with the CNF-POSS nanopaper do not decrease as expected. Even 90% weight of the nanopaper is composed by POSS. The addition of POSS particles to the nanopaper has an adverse effect, which could be attributed to the fact that the type of POSS particles used in this study has low thermal stability and they readily to migrate and sublimate during combustion.

A significant decrease in PHRR is observed for the composite laminates coated with CNF-clay nanopaper. The PHRR is decreased by 67% compared to that of the control sample. Unlike POSS particles, the thermal stability of clay is much higher. The char materials that been obtained from cone tests vary in appearance and shape, depending on the composition of composite samples. The cracks are observed in the char of the composites coated with POSS-CNF nanopapers while the char of CNF-clay nanocomposites forms a compact protective layer, which could effectively limit the transmission of heat and the supply of flammable fuels. To sum up, based on the preliminary results been presented above, it seems that the CNF-clay nanopapers are more effective than CNF-POSS nanopapers in decreasing the PHRR of composite laminates.
CHAPTER 4
FIRE PERFORMANCE OF FRPC COATED WITH CNF-CLAY HYBRID NANOPAPERS

4.1. Introduction

As the preceding chapter indicates that the CNF-clay nanopapers are very effective to reduce the PHRR of composite materials. In this chapter, more detailed work will be conducted to evaluate the fire retardant mechanisms of CNF-clay nanopapers.

Most of natural clay, known as Bentonite is originated from the alternation and/or deposition of volcanic ash. In some cases, natural clay can also be obtained by the hydrothermal alteration of volcanic rocks. The main content of natural clay is montmorillonite which is dominated by silica. As shown in figure 33, the montmorillonite essentially is layered structure which contains tetrahedral silicate layer and octahedral alumina layer. In the silicate layer, a hexagonal network is formed by linking the SiO₄ groups, composing a repeating unite of Si₄O₁₀. In the alumina octahedral layer, aluminum atoms are imbedded into the center of gallery formed by two layers of closely packed oxygen or hydroxyl. The octahedral layer shares their apex oxygen with the tetrahedral silicate layer and together they form a sandwich like structure. When in its natural state, the montmorillonite nanoclay contains Na⁺ cation as shown in the figure. In general the thickness of one sandwich
layer is approximately 0.96nm and the chemical formula of the montmorillonite clay is

$$\text{Na}_{1/3}(\text{Al}_{5/3}\text{Mg}_{1/3})\text{Si}_4\text{O}_{10}(\text{OH})_2.$$ 

Because of the hydrophilic property of natural clay platelets, it is very important to modify
them organically before disperse them into polymer. Otherwise, it is impossible to obtain the
intercalated or exfoliated dispersion, rendering the size of clay particles no longer “nano” and
their effect on the desired property will be greatly weakened.

Organic treatment is typically accomplished by exchanging the inorganic cations (such as
$\text{Na}^+$) with the desired organic cations. In this case, hundreds types of organically modified
clay have been launched commercially. For instance, Cloisite 20A supplied by Southern Clay
Products (SCP) is the natural montmorillonite modified with a quaternary ammonium salt.
The product is designed to improve the reinforcement, coefficient of linear thermal expansion
(CLTE), heat deflection temperature (HDT) and barrier properties of plastics.

Organically modified nanoclay is the most widely investigated nanoparticles and generally
speaking, it shows better efficiency in reducing the flammability of polymer than natural clay
when both of them are independently mixed with polymer. However the previous chapter indicates that when natural clay is incorporated into the hybrid nanopaper system, a dramatic reduction in PHRR of nanocomposites is observed. Therefore, in this chapter, two types of hybrid nanopapers are prepared. After coating them onto the surface of FRPC, the fire performance is examined and analyzed by TGA, Cone Tests and Microscale Combustion Calorimeter Test. In addition, the structures of these hybrid nanopapers are analyzed by SEM both before and after coated onto the surface of FRPC. According to the results of SEM analysis, the structure of hybrid nanopaper after coating is schematically showed in the figure 30. The figure indicates that both the polymer and CNF networks serve as a medium to retain the planar clay particles. Thereafter, the mechanism of flame resistance of CNF and natural or modified clay hybrid nanopapers are discussed and compared in this chapter.

Figure 34 Schematic diagram of the structure of CNF-clay hybrid nanopapers after been coated onto the surface of FRPC.
4.2. Experiment Method

4.2.1. Materials

Vapor grown carbon nanofibers (Polygraf III, PR-25-HHT) are supplied by Applied Sciences, Inc. (ASI, Cedarville, Ohio, USA) with a diameter of 50-100 nm and a length of 30–100 μm. The Cloisite Na⁺ clay is in the pure and non-modified form of montmorillonite clay. The Cloisite 20A clay is organically modified with dimethyl dehydrogenated tallow quaternary ammonium. Both are obtained from Southern Clay Products, Inc., Gonzales, Texas, USA. The glass fiber is supplied from Composites One, Inc. with a surface density of 800 g/m². The unsaturated polyester resin (product code: 712–6117, Eastman Chemical Company) is used as matrix material for laminated composites using the MEK peroxide as hardener at a weight ratio of 100:1.

4.2.2. Processing of hybrid nanopapers and nanocomposites

The as-received CNFs and clay powder was mixed and dispersed in distilled water with an aid of the surfactant Triton-X100. The mixture was then sonicated using a high intensity sonicator (600-watt Sonicator 3000 supplied by Misonix Inc., Farmingdale, New York, USA) for 30 min at a power level of 30-50 watts. After that, the suspension was filtered under a high-pressure compressed air system to fabricate the nanopaper. The as-prepared nanopaper was dried in an oven at 120 °C for 2 h. In this study, two kinds of hybrid nanopapers (CNFs with natural clay (MMT) and CNFs with organically modified clay (OMT)) were fabricated.
with different weight ratios as listed in Table 9.

<table>
<thead>
<tr>
<th>Nanocomposite sample ID</th>
<th>Contents (wt %)</th>
<th>Weight ratios of clay in the nanopaper (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GF</td>
<td>Resin</td>
</tr>
<tr>
<td>CNF laminates</td>
<td>51.72</td>
<td>45.46</td>
</tr>
<tr>
<td>CNF-OMT25 laminates*</td>
<td>51.37</td>
<td>45.83</td>
</tr>
<tr>
<td>CNF-MMT5 laminates</td>
<td>53.86</td>
<td>43.21</td>
</tr>
<tr>
<td>CNF-MMT15 laminates</td>
<td>51.62</td>
<td>45.57</td>
</tr>
<tr>
<td>CNF-MMT25 laminates</td>
<td>52.09</td>
<td>45.07</td>
</tr>
</tbody>
</table>

* A control group of cone calorimeter test for CNF-MMT25 laminates

The RTM process was utilized to manufacture laminated composites. One layer of pure CNFs nanopaper or hybrid nanopaper was placed on the top of eight layers of glass fiber mats. The unsaturated polyester resin was then injected into the mold under a pressure of 70 psi. After the resin cured at room temperature overnight, the composites were further post-cured at 120 °C for 2 h. The final composite panel was cut into 4 circular discs with a diameter of 75±0.1 mm and a thickness of 7.3±0.1 mm using water jet. These discs were the samples to be tested for their fire resistance performance.

4.2.3. Characterization and evaluation

The nanopapers and the disc-shaped samples were characterized by SEM, EDAX, TGA, cone calorimeter test, and microscale combustion calorimeter test. The procedures were described as below.

- **Scanning Electron Microscopy**

The hybrid nanopapers and the nanopapers with the polyester resin were sputter-coated with a
conductive gold layer. The images were then obtained by a SEM machine (Zeiss Ultra –55 at 5 kV) equipped with an EDAX.

● Thermaogravimetry Analysis

The TGA instrument used in this study was TGA-Q5000 from TA Co., USA. The characterization of hybrid nanopapers and the nanopapers with the polyester resin was conducted under nitrogen atmosphere at a flow rate of 35.0 ml/min and heating rate of 20 °C/min.

● Cone Calorimeter Test

The fire retardant performance of the disc-shaped laminated composites coated with nanopapers was evaluated by cone calorimeter test at an incident heat flux of 50 kW/m² according to ASTM E1354/ISO 5660. The composite samples were wrapped in an aluminum foil before cone calorimeter test. All the discs were tested in a horizontal position with the surface coated with nanopaper directly exposed to the heat flux during cone calorimeter tests.

● Microscale Combustion Calorimeter Test

A GOVMARK MCC-2 Microscale Combustion Calorimeter (MCC) was used to study the combustion of the samples (the hybrid nanopaper with polyester resin). It was used to measure the heat release rate of milligram-sized samples. A 5-mg sample was heated up to 900 °C at a constant rate of 1°C/s with a 80 cm³/s nitrogen flowing. The volatile, anaerobic thermal degradation products in the nitrogen gas stream were mixed with a 20 cm³/min stream of pure oxygen prior to entering a 900 °C combustion furnace. The heat release rate dQ/dt (in Watts)
and the sample temperature as a function of time at a constant heating rate were measured during the MCC test. The specific heat release rate (W/g) was obtained through dividing dQ/dt by the initial sample mass. [102]

4.3. Results and Discussions

4.3.1. Morphologies of nanopapers and nanopapers infused with resin

The morphologies of hybrid nanopapers are shown in figure 35. It can be seen that CNFs are uniformly dispersed and highly tangled with each other in those nanopapers. Figure 35 (a) to (d) are taken from the top surface of the hybrid nanopapers. Among these images, the clay particles could not be observed directly even when the nanopapers have the highest concentration of clay (25wt%). However, as shown in figure 35 (e), the EDAX analysis provides an evidence of the existence of clay on the top surface of the nanopaper. The oxygen and silicone element could be identified at approximately 0.5 and 1.8 keV, respectively. Furthermore, as shown in figure 35 (f), the clay platelets can be observed at the bottom surface of the CNF-MMT-25 hybrid nanopaper, which could probably be attributed to the deposition of clay particles during the high pressure filtration process.
Figure 35 SEM images of: (a) CNF, (b) CNF-MMT5, (c) CNF-MMT15 and (d) CNF-MMT25 papers viewed from top surface; (e) EDAX of CNF-MMT25 paper when viewed from top surface; (f) CNF-MMT25 paper viewed from bottom surface.

Figure 36 shows the surface morphologies of the hybrid nanopapers after the RTM process. It is clearly showed that CNFs are still uniformly dispersed and they are more compact than those in the nanopapers where resin is not infused as shown in figure 35. The surface morphologies of figure 36 (a) to (d) indicate the resin completely penetrate the nanopapers throughout the thickness direction and fully filled the pores of the nanopapers.
4.3.2. Thermal stability of nanopapers and nanopapers infused with resin

The thermal stability of hybrid nanopapers directly affects the fire performance of composites. TGA is a suitable technique for a rapid evaluation of the thermal stability of various polymer composites. The TGA results of the selected nanopapers with the resin are showed in figure 37. In these diagrams, the temperature at where 5% weight loss occurs is defined as the initial decomposition temperature. As shown in figure 37 and table 10, the decomposition temperature of pure CNF paper with the resin (curve c) is approximately 270 °C, and the weight percentage of residue at 600 °C is 15.9%. However, the decomposition temperature of the nanopaper with resin increases to approximately 287°C when MMT (25% of mass fraction) is introduced into the nanopaper. And the residue increases significantly with increasing the loading of MMT clay within the nanopapers. For example, in the case of hybrid nanopaper with resin where the nanopaper containing 25% of MMT clay (curve a), the residue increases to 40%. It is interesting to note that the addition of OMT clay in the nanopapers will
result in the reduction in both decomposition temperature and weight fraction of residue, as shown in figure 37 and table 10. Since the decomposition temperature of Cloisite 20A is about 300 °C [103] and CNFs are extremely stable as discussed in last chapter, the decrease in the decomposition temperature of the hybrid nanopaper might due to the presence of the surfactant which is relatively unstable. [104] Indeed, this is possible for the nanopapers containing OMT if one considered the organic nature of clay and surfactant.

<table>
<thead>
<tr>
<th>TGA Test</th>
<th>Samples</th>
<th>$T_{-5\text{wt%}}$ (°C)</th>
<th>Char (wt%)</th>
<th>@ 600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CNF with resin</td>
<td>271.2</td>
<td>15.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CNF-OMT20 with resin</td>
<td>268.4</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CNF-MMT15 with resin</td>
<td>287.0</td>
<td>29.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CNF-MMT25 with resin</td>
<td>281.5</td>
<td>40.0</td>
<td></td>
</tr>
</tbody>
</table>

Figure 37 TGA results of selected hybrid papers with resin.

The results obtained in this study are not consistent with the results that have been reported in open literatures. It is reported that the addition of OMT will increase the thermal stability of polymer/clay nanocomposites. [39-55] The clay platelets are found been intercalated or
exfoliated in polymers and formed nanostructure. And since the thermal stability of polymers tend to perform as a function of gallery space between individual clay platelets, the thermal stability of polymers will be enhanced when clay particles are presented in polymers as exfoliated or intercalated. [56] However, in this study, instead of adding clay directly into polyester resin, the MMT or OMT particles are first incorporated into the CNF nanopapers, thereafter the resin is infused into the hybrid nanopaper through RTM process. As a consequence, the intercalated or exfoliated structure in this study can be neglected comparing to results reported in the literatures. Furthermore, the existed possibility of surfactant attaching to the organically modified clay platelets provides a negative effect on the thermal stability of the hybrid nanopapers after RTM process.

4.3.3. Cone calorimeter tests of composite laminates coated with hybrid nanopapers

Figure 38 shows the plot of HRR versus time for glass fiber reinforced composite laminates coated with the hybrid nanopapers. For all these samples, the HRR increases rapidly to maximum value after ignition and falls back immediately, following by a second peak occurs at approximately 300 s. More specifically, the laminates coated with pure CNF paper shows a peak heat release rate (PHRR) of approximately 1200 kw/m$^2$ and time to ignition (TTI) of 35 seconds. However, the PHRR decreases dramatically with increase the mass fraction of MMT in hybrid nanopapers as shown in figure 38. In the case of CNF-MMT-5 laminates samples where 5 wt% clay particles are presented in the nanopaper, the PHRR is decreased to
approximately 710 kw/m² which is a 41% reduction compared to the sample coated with pure CNF nanopaper. When the fraction of clay is increased to 25%, the PHRR is further decreased to approximately 370 kw/m². These results indicate that there is a pronounced synergistic effect between the CNF and MMT particles. This is possibly due to the extremely low permeability of the nanopapers where high concentration of clay is used, which could prevent the migration of the volatilized gas to the surface to feed the flame.

However, it is found that when the MMT is introduced into the CNF paper, the TTI of the composites is decreased i.e. more easy to ignite. This phenomenon might be explained by two factors. First of all, the heat absorption property of carbon based material is very strong which causes the vicinity fuel is heated up rapidly to the ignition temperature. [67] Secondly, the barrier effect of the clay platelets in the hybrid nanopaper, preventing the heat from dissipating into the underlying structure. The external heat during the cone calorimeter is therefore even more concentrated on the surface. As a result, the TTI is decreased.

Figure 38 Cone calorimeter test results of CNF, CNF-MMT5, CNF-MMT15 and CNF-MMT25 laminates coated with hybrid nanopaper.

Figure 39 shows a comparison of fire retardant efficiency between the MMT and OMT.
Comparing to the samples coated with pure CNF nanopaper, the PHRR of the samples coated with the CNF-MMT and CNT-OMT paper is decreased by 69% to approximately 370 kW/m² and 54% to approximately 550 kW/m² respectively, as indicated in figure 38. However, figure 39 obviously suggests that the MMT particles have better effect on the improvement of the fire performance than OMT. This result is consistent with the TGA results been discussed during the preceding section.

Figure 39 A comparison of cone calorimeter test results between CNF-MMT25 and CNF-OMT25 laminates coated with hybrid nanopaper.

4.3.4. Microscale combustion calorimeter tests of composite laminates coated with hybrid nanopapers

The Microscale Combustion Calorimeter (MCC) is one of the most effective small scale methods to study the combustion properties of polymer materials. The MCC is especially useful for milligram sized samples. It uses oxygen consumption calorimeter to measure the rate and amount of heat, which is produced by complete combustion of the fuel gases generating during controlled pyrolysis of sample. [102] Figure 40 shows the results of MCC tests for the
CNF, CNF-MMT15 and CNF-MMT25 nanopapers with the resin. As shown in this figure, the PHRR of CNF paper with the resin is approximately 310 w/g. It decreases when the MMT is introduced into the nanopapers. The PHRR is decreased by approximately 32% and 48% when 15 wt% and 25 wt% MMT is incorporated into the hybrid nanopaper, respectively. These results further confirm that the addition of MMT clay in the CNF paper improves the fire performance of nanocomposites.

Figure 40 A comparison of microscale combustion calorimeter test results between CNF, CNF-MMT15 and CNF-MMT25 hybrid papers with resin.

4.4. Conclusions

In this study, the CNF-clay hybrid nanopapers are developed and coated onto the surface of glass fiber reinforced laminated composites through the RTM process. The SEM images of hybrid nanopapers show that CNFs are dispersed homogeneously. Due to the deposition of clay particles during the high pressure filtration process, the amount of clay particles are so little on the top surfaces of hybrid nanopapers that they could not be observed directly.
However, the EDAX analysis provides an evidence of the existence of clay particles. When the CNF-MMT 25 hybrid nanopaper is examined from the bottom surface, those clay particles are found to be tangled with the CNFs. The TGA test results show that the addition of MMT particles in the CNF nanopaper significantly improve the thermal stability of the nanopaper comparing to the pure CNF paper. However, the addition of OMT clay decreases the thermal stability due to the surfactant might exist in the nanopapers.

A pronounced decrease in PHRR is observed for laminated composites coated with the CNF-MMT nanopapers during cone calorimeter test. The PHRR is decreased up to 70% when the weight fraction of MMT reached 25%. Compared with the OMT, the MMT exhibits more significant effect in improving the fire performance of composite laminates. The results of MCC test further confirm that there exists a synergistic effect between the clay and CNFs. To sum up, the increase in the content of MMT clay within the hybrid nanopapers would result in an improvement of the fire performance of the nanocomposites. The enhanced fire performance is due to the low permeability of the hybrid nanopaper, which prevents the transmission of external heat to the underlying polyester resin and limits the volatile gases to the surface to feed the flame.
CHAPTER 5
CONE CALORIMETER STUDY OF FRPC COATED WITH CNF-XGNP HYBRID NANOPAPERS

5.1. Introduction

During the preceding discussion we know that there are two types of graphite have been widely studied to improve the flame resistance of polymer, namely, expandable graphite and graphite oxide. In this chapter, a new type of graphite is introduced into the CNF-hybrid system, i.e. exfoliated graphite nano platelets or xGnP. The chemical structure and properties of xGnP is shown in figure 41. [105]

![Structure and general properties of exfoliated graphite nano platelets. (courtesy of Drzal)](image)

* xGnP = Exfoliated Graphite Nano Platelets

- Layered Natural Mineral
- Layers can be intercalated with alkalis, acids, salts, etc. and exfoliated into nanosize platelets with high aspect ratio
- Basal Plane is a graphene sheet and inert (sp² + π)-identical to the wall of a carbon nanotube
- Existence of functional groups at the edges can lead hydrogen or covalent bond with polymer matrix
- xGnP + Polymer = Nanocomposite property improvement expected: mechanical, electrical, thermal and barrier properties

Similar to clay platelets, xGnP also has a layered structure. Therefore, intercalated or
exfoliated dispersion in polymer can be achieved by proper processing method. According to a report from Drzal et al, [105] the tensile modulus of xGnP is about 1 TPa which is as stronger as CNT. Even though it has similar planar structure as clay, the mechanic properties of xGnP are superior. Besides its higher elastic modulus, the tensile strength of xGnP is about 10 to 20 time higher and density is more than 30% lower than that clay. As a result, the mechanic properties of polymer might be better enhanced when incorporate xGnP.

In fact, Drzal et al had conducted the experiment of comparing the flexural modulus of Epon 828 with control graphite, Epon 828 with organically modified clay and Epon 828 with xGnP below and above T_g. The results as shown in figure 42 indicating a better mechanical property of polymer with xGnP. [105]

![Figure 42 Effect on flexural modulus of Epon 828 with different fillers.](courtesy of Drzal)

Furthermore, according to Drzal et al, the thermal conductivity of xGnP measured in parallel direction is 3000 W/m K while the value in perpendicular direction is 6 W/m K, a 500 time difference. And the mechanism of decreasing in permeability of polymer incorporated with xGnP is schematically shown in figure 43. [105]
In general, it is expected that the application of xGnP would lead to the enhancements in stiffness, toughness, mass reduction, electrical and thermal conductivity, barrier and scratch resistance of composite materials.

It is widely agreed that only incorporate nanofillers into polymer will not 100% satisfied the requirement of fire regulations. The traditional additives so far could not be abandoned completely. Therefore, in this chapter, the flammability of nanocomposites containing different loading of xGnP and ammonium polyphosphate (APP) are examined. As a consequence, the optimized loading of mixing is defined. After that the hybrid nanopapers combining CNFs with xGnP are fabricated. The hybrid nanopapers are then coated onto the surface of glass fiber reinforced polymer matrix composites through RTM process. Finally, the flammability of nanocomposites coated with hybrid paper are tested and discussed. The purpose of apply xGnP into CNF hybrid system is try to take advantages of its unique barrier property and thermal conductivity.
5.2. Experiment Method

5.2.1. Materials

Vapor grown carbon nanofibers (Polygraf III PR25-PS) are supplied by Applied Sciences, Inc. with a diameter of 50-100nm and a length of 30–100 μm. The xGnP is obtained from XG Sciences and APP (AP423) is supplied from Clariant International Ltd. The glass fiber (GF) is supplied from Composites One, Inc. with a surface density of 800 g/m². The unsaturated polyester resin (product code: 712–6117, Eastman Chemical Company) was used as matrix material for laminated composites with the MEK peroxide as hardener at a weight ratio of 100:1.

5.2.2. Processing of nanocomposites containing xGnP and APP

Due to the fact that it is difficult to satisfy many flame retardant regulations simply by adding nanoparticles into polymers, in this study the conventional intumescent flame retardant APP is also incorporated into polymer matrix besides xGnP. Before mixing with unsaturated polyester, xGnP is first treated by acetone in order to improve its wettability with resin. Specifically, xGnP powders are suspended in acetone and then the mixture is sonicated by a high intensity sonicator (600-watt Sonicator 3000 from Misonix Inc.) with a power of 90 watts for 20 min. After that, the acetone is removed by vacuum pump, leaving relatively dry xGnP powders behind. Finally, the treated xGnP and as received APP are mixed into unsaturated polyester by a mechanical mixer for 2.5 hours. After preparing polymer, resin
transfer molding (RTM) process is used to manufacture glass fiber reinforced nanocomposites, i.e. the polymer is injected into an aluminum mold under an 80psi pressure. In the mold, there are eight layers of glass fiber mats. After resin is cured within the mold at room temperature for overnight, the composites are further post-cured at 120 °C in an oven for 2 hours. Thereafter, the sample is ready to be cut into circular discs for cone calorimeter tests. Table 11 shows the composition of xGnP nanocomposites samples.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Contents (wt %)</th>
<th>Weight ratios of GNP/APP/Resin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>xGnP-APP-0-laminates</td>
<td>51.75 48.25 0</td>
<td>0/0/100</td>
</tr>
<tr>
<td>xGnP-APP-15-laminates</td>
<td>48.23 41.41 10.35</td>
<td>5/15/80</td>
</tr>
<tr>
<td>xGnP-APP-17-laminates</td>
<td>49.18 40.66 10.16</td>
<td>3/17/80</td>
</tr>
<tr>
<td>xGnP-APP-18-laminates</td>
<td>47.30 42.16 10.54</td>
<td>2/18/80</td>
</tr>
<tr>
<td>xGnP-APP-19-laminates</td>
<td>49.78 40.18 10.04</td>
<td>1/19/80</td>
</tr>
<tr>
<td>xGnP-APP-20-laminates</td>
<td>50.71 39.43 9.86</td>
<td>0/20/80</td>
</tr>
</tbody>
</table>

5.2.3. Processing of hybrid nanopapers and nanocomposites

After first stage experiment, an optimized ratio of xGnP, APP and resin mixture is acquired which exhibits the best flame resistance. During the second stage research, the pre-existed char layer, i.e. xGnP and CNF hybrid papers are designed and coated onto the surface of nanocomposites. The as-received CNF, xGnP and their mixture are dispersed in dispersed independently in distilled water. The mixed suspension is sonicated for 30 min with a power of 30-50 watts. It is important to note, before sonication process, the surfactant Triton-X100
is added in to the suspension to ensure the homogenous dispersion. After the well dispersed suspension is obtained, the pure and hybrid nanopapers are fabricated by filtering the suspension through a high pressure compressed air system. Then nanocomposites coated with pure/hybrid papers are fabricated by RTM during where one layer of nanopaper is placed on the male half of aluminum mold and eight layers of glass fiber mats are fitted in the female half of the mold. During the cone calorimeter tests, the surfaces of sample discs coated with nanopaper are directly exposed to heat flux. The composition of hybrid nanopapers and nanocomposites is shown in table 12.

<table>
<thead>
<tr>
<th>Nanocomposite sample ID</th>
<th>GF</th>
<th>Resin</th>
<th>xGnP</th>
<th>APP</th>
<th>Nanopaper</th>
<th>Weight ratios in the nanopaper</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA-L</td>
<td>49.83</td>
<td>40.14</td>
<td>2.01</td>
<td>8.03</td>
<td>0</td>
<td>no paper</td>
</tr>
<tr>
<td>C0G1-GA-L</td>
<td>50.17</td>
<td>38.91</td>
<td>2.19</td>
<td>8.74</td>
<td>1.20</td>
<td>CNF/xGnP = 0/1</td>
</tr>
<tr>
<td>C1G3-GA-L</td>
<td>49.16</td>
<td>39.73</td>
<td>2.22</td>
<td>8.89</td>
<td>1.17</td>
<td>CNF/xGnP = 1/3</td>
</tr>
<tr>
<td>C1G1-GA-L</td>
<td>48.12</td>
<td>40.59</td>
<td>2.26</td>
<td>9.04</td>
<td>1.15</td>
<td>CNF/xGnP = 1/1</td>
</tr>
<tr>
<td>C3G1-GA-L</td>
<td>48.85</td>
<td>39.99</td>
<td>2.23</td>
<td>8.93</td>
<td>1.17</td>
<td>CNF/xGnP = 3/1</td>
</tr>
<tr>
<td>C1G0-GA-L</td>
<td>48.27</td>
<td>40.46</td>
<td>2.25</td>
<td>9.02</td>
<td>1.15</td>
<td>CNF/xGnP = 1/0</td>
</tr>
</tbody>
</table>

5.2.4. Characterization and evaluation

- **Scanning Electron Microscopy**

  The hybrid nanopapers and char materials after cone calorimeter test were sputter-coated with a conductive gold layer. Then they were analyzed by a Zeiss Ultra –55 SEM machine at 5 kV.

- **Con Calorimeter Tests**
The fire retardant performance of the nanocomposites before and after coated with nanopapers was evaluated by cone calorimeter test at an incident heat flux of 50 kW/m² according to ASTM E1354/ISO 5660. The composite samples were wrapped in an aluminum foil before cone calorimeter test. All the samples were evaluated in a horizontal position with the surfaces coated with nanopapers directly exposed to the heat flux during cone calorimeter tests.

5.3. Results and Discussions

5.3.1. Cone Calorimeter test of nanocomposites containing xGnP and APP

Direct results from cone calorimeter tests

The heat release rates (HRR) of materials obtained by cone calorimeter tests are the most important bench scale parameter to study the fire performance of the materials. The HHR is determined by the oxygen consumed during combustion due to the fact that all most every material produces 13.1 MJ heat when 1 kg of oxygen is consumed during combustion reaction. Figure 44 shows the heat release rate results of the samples illustrated in table 11. For the sake of simplicity, APP0 is the xGnP-APP-0-laminates sample and similarly, APP20 is the xGnP-APP-20-laminates sample. The same rule also applies to other data and figures in this chapter. General speaking, the patterns of the HRR figure indicates that these samples are thermally thick charring material. Before the char layer is formed, there is a peak occurs
in the initial stage of combustion reaction. It is clear that almost at the end of the combustion process around 350 seconds, there is a second peak appears which might due to the cracking of char layer and/or the increase of effective degradation of polymer (as shown is figure 44). [106] For all this samples, when the resin matrix contains APP and/or xGnP, more or less there is a decrease in PHRR comparing to the APP0 sample where no xGnP or APP is incorporated. And the one mixed with 18wt% of APP and 2wt% of xGnP in the unsaturated polyester shows the lowest PHRR which is more than 40% reduction comparing to the APP0 sample. In addition, when the loading of xGnP is greater and 2% i.e. APP is lower than 18% the PHRR became higher and the reduction of PHRR drops to 30% for the APP20 sample. The same thing happens when decrease the loading of xGnP. If one further examines the trend of the decrease or increase of PHRR, the figure suggests that there exists an optimized ratio between APP and xGnP provided that the total weight percentage of additives in resin is 20%. The existence of optimized ratio also indicates that under such a ratio, the synergistic effect between APP and xGnP is best revealed. More specifically, the planar structure of xGnP reduced the permeability of melted structure as well as char and thus the enhancement of barrier effect achieved in this case. Moreover, during the process of mixing xGnP and APP with resin, the nanoscaled xGnP would increase the viscosity of parent resin which provides a preferred environment to form a high quality char. [79] Meanwhile, the relatively large amount of traditional intumescent flame retardant APP will not only stimulate the char forming process, but also reduce the thermal conductivity of the char caused by the
production of foaming structure (figure 46). As a result of synergistic effect between xGnP and CNFs, the low thermal conductivity and permeability char layer will dramatically decrease the flammability of composite materials.

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**Figure 44** Heat release rate of nanocomposites discs with different concentration of xGnP and APP in resin (Time range: right, 0~800s; left 0~100s).

**Figure 45** Mass loss rate of xGnP-APP-17-laminates, xGnP-APP-18-laminates and xGnP-APP-20-laminates.
The incorporation of xGnP and APP into polymer matrix not only influences the PHRR, but also has a significant effect on total mass loss (ML) and thus the weight of char yielding. As listed in table 13, the sample exhibits lowest PHRR also shows the most weight percentage char yielding and lowest mass loss. And those samples contained xGnP and/or APP without exception show increased char yielding and decrease in mass loss which coincide with the heat release rate pattern mentioned above. It is important to note that since the polymer is reinforced by glass fiber mats which are inflammable, even though the polymer of APP0 sample is completely consumed during combustion reaction process, the weight percentage of mass loss is not 100%. Based on the data of table 13, an interesting phenomena is that although comparing to the control sample where no APP or xGnP is incorporated, there is a reduction in total heat released (THR) for these samples containing xGnP and/or APP, the difference of the reduction between the samples is very small which
indicates that the relatively large amount of APP might dominate the THR. This in fact suggests that in order to truly improve the fire performance of composite materials, traditional flame retardant is indispensable.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Time to ignition(s)</th>
<th>PHRR (kw/m²)</th>
<th>Time to PHRR(s)</th>
<th>Total Heat Released (MJ/m²)</th>
<th>Mass Loss (wt%)</th>
<th>Char Yielding (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>xGnP-APP-0-laminates</td>
<td>44</td>
<td>420.67</td>
<td>60</td>
<td>134.90</td>
<td>49.34</td>
<td>0</td>
</tr>
<tr>
<td>xGnP-APP-15-laminates</td>
<td>43</td>
<td>379.70</td>
<td>75</td>
<td>110.78</td>
<td>42.95</td>
<td>9.83</td>
</tr>
<tr>
<td>xGnP-APP-17-laminates</td>
<td>51</td>
<td>295.40</td>
<td>80</td>
<td>115.62</td>
<td>43.15</td>
<td>8.70</td>
</tr>
<tr>
<td>xGnP-APP-18-laminates</td>
<td>46</td>
<td>251.94</td>
<td>65</td>
<td>106.66</td>
<td>37.97</td>
<td>15.72</td>
</tr>
<tr>
<td>xGnP-APP-19-laminates</td>
<td>35</td>
<td>292.28</td>
<td>70</td>
<td>117.00</td>
<td>42.98</td>
<td>8.29</td>
</tr>
<tr>
<td>xGnP-APP-20-laminates</td>
<td>48</td>
<td>296.49</td>
<td>70</td>
<td>115.31</td>
<td>44.14</td>
<td>6.22</td>
</tr>
</tbody>
</table>

Since one of the most important objective of this thesis is trying to find a well behaved pre-exist char to protect the underlying structure at very beginning, it is necessary to assess the fire performance of composites coated with hybrid nanopaper systems. The heat release rate of such samples listed in table 12 is shown in the figure 47. Similar to those thermally thick charring materials, the HHR curves of the samples coated with hybrid nanopapers also exhibit two peaks in the initial and end stage of combustion reaction. In other words, these hybrid papers indeed serve as char layers when the samples are exposed to heat flux. Moreover, as listed in table 14, the TTI of those samples coated with nanopapers containing xGnP are delayed up to 52% comparing to the control sample where no paper is used or the sample coated with pure CNF paper. Such a result demonstrates that the planar structure of xGnP in the pre-existed char layer plays an important role to prevent the mass flow of fuels.
originating from the decomposition of polyester resin. Especially when consider the case where pure xGnP paper is used, both TTI and time to PHRR are delayed. Another interesting phenomenon is that when comparing to the control sample, although there is an increment in THR for the samples coated with nanopapers, the percentage of such increment is relatively small, about 0~10%. That is by keeping the constancy of APP within resin, the changing of weight ratio of xGnP/CNF has very limit effect on THR of samples, which again indicates that the traditional flame retardant APP have more influence on the THR than xGnP.

Figure 47 Heat release rate of nanocomposites discs coated with different types of hybrid/pure nanopapers with 2% of xGnP and 18% of APP in resin (Time range:right,0~800s; left 0~100s).

However, all those samples coated with pure or hybrid nanopapers show an increment in PHRR, Mass Loss percentage, and Char Yielding rate as listed in table 14. Additionally, the samples coated with hybrid and pure CNF nanopapers show an increase in THR. In order to address these phenomena, it is necessary to revisit the function of an idealized HRR during a “steady-state” burning, i.e. $HRR = \chi (1-\mu)(h_c^0/h_g)(dq_{ex}+dq_{flame}-dq_{cond}-dq_{re-radiated})$, in which

$\chi$ is the combustion efficiency
\[ \mu \text{ is the residue yield} \]

\[ h_{c}^{0} \text{ is the effective heat of combustion} \]

\[ h_{g} \text{ is the heat of gasification.}[106] \]

According to the above equation, besides the effect of char yield which directly relate to mass loss, the conducted and re-radiated rate of heat also influence the heat release rate.

1. Increase in THR, mass loss and char yielding.

The consequence is determined by multiple factors that occur simultaneously. One possible factor is due to the absorption characteristic of the carbon based nanopapers. [67] There is an extremely high concentration of the carbon based materials on the surface of the sample that is coated with nanopaper which absorbs heat from external radiation. As a result, the surface of the sample is heated up in a rapid pace and the resin in the vicinity of the nanopaper is degraded relatively easy. Thus more fuel is likely to be released, involving in the combustion reaction. Meanwhile, the thermal conductivity of CNT and xGnP are 20~2000W/m K and 6-3000W/m K [105] respectively depending on their orientations, which are much higher than polymers. As a result, the heat will be conducted easily and the HRR of the sample will be reduced. As a consequence of these multiple effects, there is an increase in THR and total mass loss, however, the increment relatively small.

2. Increase in PHRR.

By the virtue of barrier effect of xGnP, even though the resin is readily to be pyrolyzed, the rate of fuel immigration is low which is directly demonstrated by the reduction of smoke
production rate where pure xGnP nanopaper is used as shown in figure 48. Therefore, the TTI and time to PHRR is delayed or unchanged. And the concentration of the fuel in gas state above the surface of a sample is expected to be high in such a low immigration rate when the PHRR occurs, thus the PHRR will increase due to the large consumption of oxygen.

Table 14 TTI, PHRR, Time to PHRR, THR Mass Loss and Char yielding of nanocomposites discs coated with different types of nanopapers.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Time to ignition (s)</th>
<th>PHRR (kw/m²)</th>
<th>Time to PHRR (s)</th>
<th>Total HRR (MJ/m²)</th>
<th>Mass Loss (wt %)</th>
<th>Char Yielding (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA-L</td>
<td>46</td>
<td>265.35</td>
<td>70</td>
<td>107.19</td>
<td>35.10</td>
<td>17.95</td>
</tr>
<tr>
<td>C0G1-GA-L</td>
<td>70</td>
<td>325.03</td>
<td>75</td>
<td>106.25</td>
<td>38.68</td>
<td>11.16</td>
</tr>
<tr>
<td>C1G3-GA-L</td>
<td>56</td>
<td>395.91</td>
<td>65</td>
<td>114.46</td>
<td>43.51</td>
<td>7.34</td>
</tr>
<tr>
<td>C1G1-GA-L</td>
<td>48</td>
<td>401.34</td>
<td>65</td>
<td>119.76</td>
<td>42.44</td>
<td>9.44</td>
</tr>
<tr>
<td>C3G1-GA-L</td>
<td>51</td>
<td>404.44</td>
<td>70</td>
<td>116.09</td>
<td>41.17</td>
<td>9.99</td>
</tr>
<tr>
<td>C1G0-GA-L</td>
<td>46</td>
<td>432.69</td>
<td>65</td>
<td>117.68</td>
<td>43.19</td>
<td>8.51</td>
</tr>
</tbody>
</table>

Figure 48 Smoke production rate of GA-L, C0G1-GA-L and C1G0-GA-L samples.

Deduced results from cone calorimeter tests

It seems that there is no clearly influence of only incorporating APP and/or xGnP into polymer on the time to ignition (TTI) and time to PHRR (table 13). However, this data can be
useful when consider fire growth rate index (FIGRA) for regulatory purpose, end-use conditions, reproducibility and unambiguous data evaluation. [106] Specifically, fire growth rate index (FIGRA) is calculated by dividing the PHRR with the time at which this occurs. The values of FIGRA versus different samples are plotted in figure 49. As shown in the figure, a sample that has low FIGRA value might be defined as good flame resistant sample. A slightly different from the HRR curve, for the mixing group, the sample that containing 17% of APP and 3% of xGnP in its resin shows best fire performance; for the paper-coating group, the nanopapers seems improve the flammability of the samples.

![Figure 49 FIGRA values of samples with/without nanopaper.](image)

It is widely accepted that the greatest influence on the fire hazard are the fire load and flame spread. However, since flame spread is not readily to be measured, Petrella proposed that the value of THR, PHRR/TTI obtained from cone calorimeter tests can be used to represent fire load and flame propagation respectively.[107] Figure 50 plots the THR against PHRR/TTI. It is clear that the closer the data to origin, the better char quality or flame retardant property of the sample will be. The results of the left figure have very high degree
of coincidence with the HRR curve while the right figure indicates that sample coated with pure xGnP paper exhibits lowest flammability.

![Figure 50 THR versus PHRR/TTI for different samples.](image)

If one considers the equation to calculate HRR, the char yielding rate $\mu$ and effective heat of combustion of the vaporized mass $h_c^0$ are two important intrinsic material properties. Therefore, in order to better confirm or rank the flammability of different samples, plotting the THR versus total mass loss would be an effective approach. [106] Such a plot is showed in figure 51. It is suggested that when incorporating 2% of xGnP and 18% of APP into resin, both THR and mass loss are dramatically reduced comparing with the sample which containing no additives within resin. And, the coating pure xGnP nanopaper will result in a slight decrease in THR of the sample. Otherwise, both the THR and mass loss will increase comparing to the sample without any coatings.
To sum up the above deduced results, it seems that APP18 of the mixing group and GA-L and C0G1-GA-L of the paper-coating group exhibits the best flame resistance property. However, it is important to note that a combustion reaction process is extremely complicated which is influenced by the thickness and deformation of specimen, physical and chemical mechanisms and environmental condition during the process. [106] Only the direct data or deduced value from cone calorimeter test should not sufficient enough to determine the fire performance of certain material.

5.3.2. Morphology of the nanopapers and char materials after cone calorimeter tests

A deep insight into the flame retardant mechanism of different samples is permitted by analyzes the char materials after cone calorimeter tests.

Morphology of the nanopapers

The morphology of nanopaper before coating onto the surface of FRPC is showed in figure 52. Images (a) and (b) indicate that the xGnP particles are well dispersed and tangled in CNFs.
networks. Intuitively, when the loading of xGnP is increased within hybrid nanopapers, the permeability of the nanopapers will decrease due to the fact that xGnP particles are filled into the pores of CNFs networks.

Figure 52 SEM images of nanopapers: (a) C1G3 (b) C3G1 (c) C0G1.

Morphology of chars obtained after cone calorimeter tests

Figure 53(a), (b) and (c) show the char characteristics of xGnP-APP-15-laminates, xGnP-APP-18-laminates and xGnP-APP-20-laminates respectively after cone calorimeter tests. They indicate that during the combustion process, the sample with 2% of xGnP and
18% of APP in its resin will form a char layer with compact surface while there are large amount of pores and cracks within the char of APP15 sample and cracks within the char of APP20. As a result, the high quality of APP18 char layer has a best effect on the fuel immigration, reducing the PHRR, THR and total mass loss of the nanocomposites during cone tests.

Figure 53 Char SEM image of (a) xGnP-APP-15-laminates, (b) xGnP-APP-18-laminates, (c)xGnP-APP-20-laminates.

Figure 54 and 55 show the char characteristics of the composites coated with nanopapers obtained after cone calorimeter test. There are three types of char formed during combustion...
reaction, namely, A type, B type and C type as shown in the figures. It is clear that A type of char is the most compact while the C type char is the loosest one. Coincide with the previous discussion, the sample C0G1-GA-L shows largest amount of A type chars in the surface and thus has the best flame resistance (figure 54). However, most of the chars from sample C1G0-GA-L are composed by type B and C (figure 55), therefore shows the lowest flame resistance. Nevertheless, both of these two samples possess a char layer that is looser than that of the xGnP-APP-18-laminates sample as shown in figure 53 (b), indicating a higher flammability.

Figure 54 Char SEM image of sample C0G1-GA-L.
5.4. Conclusions

By thorough analysis of cone calorimeter test data and in the aid of SEM, it is found that thermal conductivity of composites and char, heat absorption, re-radiation and permeability of char play important role in determining the flammability of the materials. XGnP particles as alternative to clays show excellent barrier effect when they are mixed in polymers and incorporated into CNFs nanopapers. More specifically, when proper ratio of xGnP and APP particles are mixed with the polyester resin, the PHRR, total mass loss and THR are greatly decreased. When xGnP particles are incorporated into CNFs nanopapers, the TTI and time to
PHRR is delayed due to their barrier effect. Furthermore, the thermal conductivity of the polymers and hybrid nanopapers is improved which is preferred to enhance the flame resistance of polymer, but not necessary good for hybrid nanopapers. Moreover, the traditional flame retardants APP are proved to be important to control the total heat release of composite materials during combustion reaction process.

In order to achieve better flame retardancy, it is preferred to improve the thermal conductivity of the whole composite laminates and to reduce the permeability, heat absorption of the char if existed.

5.5. Flame Resistance Behavior of FRPC Coated With CNF/APP/Clay Hybrid Nanopapers

As mentioned in previous discussions, in order for charring composite materials to improve their flame resistance it is necessary to obtain high quality char layers. These char layers should possess the following characteristics:

1. They should be tough enough to resist cracking during combustion process.

2. The thermal conductivity of the char in thickness direction should be low, slowing down the process of degradation of the underlying polymer (such as foaming and porous structure char).

3. The in-plane thermal conductivity of the char should be high, dissipating the heat being absorbed.

4. The permeability of the char should be low enough to prevent the migration of fuel
originating from the pyrolysis of the polymer from feeding the flame, but not so low as to induce a strong repelling force, which is generated by the gas phase fuel beneath the char layer.

Based on these experiences another type of hybrid paper was recently developed, CNF/APP/Clay hybrid nanopaper. As shown in figure 56, the extremely thermal stable CNFs still serve as the structure to hold particles in this type of nanopaper. The clay that used in this hybrid system is a type of natural clay whose main function is reducing the permeability of hybrid nanopapers, yet it is easy to disperse within the CNFs networks and exhibits high thermal stability. The APP particles in the hybrid system serve as blow agent. When the composites that are coated with this type of hybrid nanopapers undergo external heat flux, the blow agents are expected to generate air bubbles within the char structure, swelling up the protective layer. As a result, the thermal conductivity in the thickness direction will be greatly reduced. Additionally, APP itself is a very effective intumescent flame retardant that will further enhance the flame resistance efficiency of the hybrid nanopaper.

Figure 56 Structure of CNF/APP/clay hybrid nanopaper and its behavior under external heat radiation.
During the experiment, five types of composite materials were prepared as listed in table 15. There was no paper coating on the control sample and there were no additives in the resin of any of the samples.

Table 15 Composition of CNF/APP/clay hybrid nanopapers and nanocomposites.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Contents (wt %)</th>
<th>Weight ratios of CNF/Clay/APP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GF</td>
<td>Resin</td>
</tr>
<tr>
<td>Control</td>
<td>44.19</td>
<td>55.80</td>
</tr>
<tr>
<td>C5Y3A7</td>
<td>48.21</td>
<td>49.46</td>
</tr>
<tr>
<td>C5Y2A8</td>
<td>50.23</td>
<td>47.34</td>
</tr>
<tr>
<td>C5Y1A9</td>
<td>46.12</td>
<td>51.64</td>
</tr>
<tr>
<td>C5Y0A10</td>
<td>49.05</td>
<td>48.57</td>
</tr>
</tbody>
</table>

Figure 57 shows the heat release rate curves of the samples during cone calorimeter test. Generally speaking, all the samples coated with hybrid papers containing APP indicate better flammability resistance than the samples without any coating (black line). Moreover, they all exhibit two peaks during cone test, unlike the control sample. The first peak indicates the start of fully developed fire and the second peak may indicate the cracking of char and/or increase in the effective pyrolysis near the end stage of combustion reaction. [106]
As shown in figure 58, the first peaks of the samples coated with hybrid nanopapers are much lower than the control sample. The reductions are from 20% up to more than 50%. However, the time to the first peak heat release rate and time to ignition for the samples coated with hybrid nanopapers are shortened due to the relatively strong heat absorption ability of CNFs structure. [67]
Table 16 lists the detailed cone test data of these samples. It seems that when the APP content of the hybrid nanopaper is increased, the time to ignition is delayed, indicating that APP contributes more to reducing the heat absorption ability of hybrid nanopaper than natural clay. Furthermore, when compared with C5Y0A10 sample, where no clay particles are present, the samples coated with clay-containing hybrid nanopapers show lower 1\textsuperscript{st} and 2\textsuperscript{nd} peak heat release rates, which indicate the planar structure of clay particles effectively retard the migration of fuel to feed flame, keeping the concentration of fuel around the combustion zone at a lower value than that C5Y0A10 sample. The further investigation of the 1\textsuperscript{st} PHRR indicates that there exists an optimized ratio of CNF, clay, and APP concentrations of the hybrid system that results in the lowest 1\textsuperscript{st} PHRR i.e. CNF/clay/APP=5/2/8. This interesting phenomenon might be attributed to the competing mechanisms lowering the permeability of nanopapers with the planar structure of clay and lowering the thermal conductivity with the blow agent APP. In other words, blow agent generates air bubbles that will lower the thickness thermal conductivity and increase the permeability of hybrid nanopaper; but clay particles decrease the permeability of nanopaper and tend to inhibit the formation of air bubbles within the nanopaper during combustion. In the case of long term data such as 2\textsuperscript{nd} PHRR, THR, mass loss, and char yield, the trend is relatively unclear among those samples coated with hybrid nanopaper due to the fact that combustion reaction is unstable and the weight percentages of nanoparticles within the samples are very small. However, one certainty is that all the data indicates that the flammability of the FRPC is reduced with a
coating of hybrid nanopaper.

Table 16 Detailed cone calorimeter test data of FRPC coated with/without CNF/APP/caly hybrid nanopapers.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Time to ignition (s)</th>
<th>1st PHRR (kw/m²)</th>
<th>2nd PHRR (kw/m²)</th>
<th>THR (MJ/m²)</th>
<th>Mass Loss (wt %)</th>
<th>Char Yielding (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>43</td>
<td>486.68</td>
<td>471.48</td>
<td>82.55</td>
<td>55.80</td>
<td>0</td>
</tr>
<tr>
<td>C5Y3A7</td>
<td>19</td>
<td>335.98</td>
<td>412.14</td>
<td>76.57</td>
<td>50.74</td>
<td>2.27</td>
</tr>
<tr>
<td>C5Y2A8</td>
<td>21</td>
<td>230.26</td>
<td>368.14</td>
<td>67.14</td>
<td>46.08</td>
<td>3.67</td>
</tr>
<tr>
<td>C5Y1A9</td>
<td>34</td>
<td>268.46</td>
<td>347.12</td>
<td>79.80</td>
<td>51.15</td>
<td>2.71</td>
</tr>
<tr>
<td>C5Y0A10</td>
<td>36</td>
<td>390.37</td>
<td>429.48</td>
<td>71.04</td>
<td>46.40</td>
<td>4.71</td>
</tr>
</tbody>
</table>
6.1. A Summary of the Previous Work

The most important objective of the previous work is to enhance the flame resistance of FRPC by seeking an effective as well as practical pre-existed protective char layer. First of all, the thermal stability of such a “char” should be extremely high which automatically leads us to seek carbon based material. After all, many literatures report a high quality and compact carbonaceous protective char layer when the nanocomposites show excellent flame resistance. The pioneering researches done by Kashiwagi et al provide us a promising idea to achieve such an aim. [79-83] In fact, initially carbon nanotube (CNT) has been tried to fabricate into buckypaper. Although it is possible to make such a CNT paper without adding any bonding agent (because the bonding agent might decrease the thermal stability of the nanopaper), the as-made buckypaper is extremely brittle due to the short length of CNT, rendering the difficult of further processing. Carbon nanofiber (CNF), however, does not exhibit such a shortcoming. Since the CNFs can tangle with each other tightly, it is relatively easy to fabricate a processible CNF paper. Moreover, the cost of CNF is much lower than CNT yet possesses similar physical properties. As a result, CNF is the ideal choice to form such a pre-exist “char layer”. Nevertheless, it is impossible to achieve flame resistance by coating
the pure CNF paper onto the surface of composites materials. In fact, Z. Zhao et al reported that when use pure CNF paper alone, the flammability of FRPC was increased instead of decreased. The PHRR of the sample was extremely high and the time to ignition was very short. In other words, the sample was not only easy to catch fire but also release huge amount of heat, providing the heat source of sustainable combustion reaction. In such a case, the CNF paper was not a “fire retardant” but only a “fire catalyst”. Therefore, as a second step, it is important to modify CNF nanopaper.

Indeed, the whole story of this thesis is focused on examining the effective of different type of hybrid CNF nanopapers. When hybrid nanopaper is coated onto the surface of composite panels, the CNF along with polymer matrix serve as media to retain those particles that are hybridized in. Therefore, a desired synergistic effect is exhibited. For example, when designing the clay-CNF hybrid paper, multiple effects are exhibited. Besides the fact that CNF will hold the clay particles, these particles themselves are very promising fire retardants. The nano distributed clay will increase the viscosity of polymer which is important to form compact char during combustion process. Furthermore, the planar structure of clay compensates the high permeability of the CNF paper which in turn plays significant role when preventing the mass flow of fuels originating from the decomposition of resin. As a consequence, the condition for sustainable flame propagation will be harmed and the fire resistance is achieved. However, the delicate interactions between clay, CNF and polymer molecular are not thoroughly understood. One thing is for sure that the efficiency of the
clay-CNF hybrid paper is far better than pure CNF paper.

Even though the hybrid systems are appreciated and preferred, the large variability in the efficiency of flame resistance exists between different types of hybrid systems. When comparing the four types of hybrid papers i.e. organic clay-CNF, pristine clay-CNF, POSS-CNF and xGnP-CNF hybrid paper, pristine clay-CNF hybrid paper shows the best effect in reduction the flammability of FRPC and is followed by POSS hybrid paper. The xGnP-CNF hybrid system almost exhibit “flame catalyst” effect. These results show that only adopting a hybrid concept alone would not automatically lead to flame resistance. It is extremely important to choose right hybrid system by fully understanding unique properties of those materials. Specifically, although the thermal stability and the structure of CNF are unbeatable, its thermal conductivity is relatively high and the pure CNF paper exhibits high permeability. It is determinant in such a case that a material is chosen to hybridize should remedy those disadvantages of pure CNF paper, namely, the material should has high heat capacity, low thermal conductivity in thickness direction and low permeability. POSS is a cage like structure, even though it might remedy the high thermal conductivity of pure CNF paper, the permeability as a whole is still high. xGnP is a planar structure material, uncompensating the high permeability of pure CNF paper, but its carbon based chemical compound makes the hybrid paper shows high thermal conductivity and heat absorption. And based on the experiment data discussed in the last chapter, the thermal effect is overwhelming in such a competing mechanism.
The pristine clay is more compatible to CNF than organically modified clay and yet the clay shows extremely low permeability during paper making process and along with its excellent thermal behavior, it is no doubt that the overall fire performance of FRPC coated with pristine clay-CNF hybrid paper is the best.

As a rule of thumb, an ideal char layer that could able to protect the underlying structure should simultaneously possess following characteristics: low thermal conductive in thickness direction and high in-planar thermal conductivity which dissipates heat quickly, high stability, low heat absorption, high heat capacity and a compact surface to prevent mass immigration. In fact, those researches that contributing the reduced flammability to high quality chars without exception have most of the above properties. For instance, the direct effect of nano-disperse additives into polymer is that the viscosity of polymer would increased, behaving solid like property (the size and properties of polymer molecular would influence such a behavior) as Kashiwagi et al mention in his research. [79-83]
Figure 59 Different behavior of PP(left) and PP mixed with 1% of MWNT(right) under gasification test. (courtesy of Kashiwagi)

As shown in figure 59, the pristine PP which shows low flame resistance in the left behaves as liquid during gasification test while the right sample in which the MWNTs are mixed behaves as solid, exhibiting high flame resistance. A possible explanation is that when such as solid like polymer is exposed to heat flux, it is expected that a continuously char would be formed. (figure 60) The char is able to prevent mass immigration, cutting off the supply chain of combustion and geometrically and thermally stable. It is important to note the continuous char should not be to compact. Since the overall compactness would render such a char extremely thermal conductive which accelerate the pyrolysis of underlying polymer. In fact, such a char always shows porous structure as shown in figure 61. As a consequence, the thermal conductivity in the thickness direction of the char layer is very low.
At this point, it is reasonable to postulate that if some blow agents such as APP were incorporated into the pristine clay-CNF hybrid nanopapers by carefully designing, the fire performance of the FRPC would be further enhanced. This work will be carried out in future research.
6.2. A Overview of the Future Work

6.2.1. Extensive tests data is needed

Throughout this thesis, Cone Calorimeter Test, TGA and SEM are the major experiments have been carried out to evaluate the fire behavior of samples. Even though PHRR is considered as a most important bench-scale parameter to determine the flammability of test sample, it is far from enough to make a final judgment of the flammability and safety of the sample. In fact, in United States comprehensive flammability test methods are defined and issued by four organizations: American Society for Testing and Materials (ASTM), Underwriters’ Laboratories (UL), National Fire Protection Association (NFPA) and International Conference of Building Officials (ICBO). Such types of tests include tests for smolder susceptibility, ignitability, flash-fire propensity, flame spread, heat release, fire endurance, ease of extinguishment, smoke evolution, toxic gas evolution and corrosive gas evolution. Each type of tests also includes various types of sub-test. For example, tests for toxic gas evolution can be carried out by approaches as infrared analysis, gas chromatography, mass spectrometry, chemiluminescence, polarographic methods, paramagnetic methods, ion-selective electrodes, titrimetric methods and colorimetric methods. [108]It seems that the cone calorimeter test for heat release rate is only a tiny component in the flammability tests family. Of course, one would never expect to do all the tests for research purpose. Yet, it is necessary to evaluate those tests, carefully choose some representing methods which will maximize the ability of helping researchers understand the flame resistance mechanism.
Besides the flammability test which is the privilege of the research, it is also necessary to conduct some mechanical evaluations. A desirable flame resistant FRPC should not scarify its mechanical advantages when the objective of reduction in flammability is realized.

6.2.2. Alignment-a new idea to achieve flame resistance

It seems that there are two factors defined the quality of char, namely, permeability and thermal conductivity. (A lower permeability and thermal conductivity in thickness direction char is preferred.) And it seems that the thermal properties such as thermal conductivity, heat absorption property and heat capacity play more important roles in combating flame propagation than permeability, which is demonstrated by comparing the case of POSS-CNF hybrid and xGnP-CNF hybrid systems. The former case possesses lower thickness direction thermal conductivity and higher permeability than that the latter case however shows low flammability. Therefore, the effect on reducing the flammability of composite materials might be remarkable when pay more attention to their thermal properties.

The work of Kashiwagi indicates that well dispersed nanotube in PP or PMMA polymer will greatly improve the flame resistance of parent polymer. In fact, E.S Choi et al report when 3wt% of SWNT is dispersed into epoxy, the increase in thermal conductivity is up to 300% with further a increasing after magnetic alignment as shown in figure 62. [109]
Figure 62 Thermal conductivity of CNT-epoxy composites magnetically processed at 0
and 25 T, compared with the neat epoxy control sample (also processed at 25 T).
The thermal gradient was applied along the magnetic field alignment direction.

However, Kashiwagi seems do not pay much attention for this effect that a drastic
increasing in thermal conductivity occurs and he only considers the case of randomly
distribution but not the case of intentionally oriented CNT distribution nanocomposites. For
example, when the majority of CNTs dispersed in polymer are perpendicular to the heat flux,
it's flammability behavior of the nanocomposite will be different to that the CNTs are parallel
to the heat flux or to that the CNTs that are randomly oriented. Actually, Fischer et al report
that the thermal conductivity of SWNT based nanocomposite in the parallel direction is up to
8 times larger than that in perpendicular direction as shown in figure 63. [110-111]
Figure 63 Thermal conductivity of annealed 7 (a) and 26 (T) aligned SWNT films (b) measured with heat flow perpendicular and parallel to the alignment axis.

As a matter of fact, the alignment of CNT and CNF in polymer under magnetic field or electric field has attracted considerable attention and extremely amazing results are reported. This technique allows researchers to exploit the anisotropic thermal, mechanical, electrical and optical properties of nanocomposites, a capability that traditional polymer process cannot provide. [112] Figure 64 shows the alignment of Vapor-Grown Carbon Fiber (VGCF) under electric field. [113] In the figure 64 (a) diagram, metal electrodes are used and the observation direction is perpendicular. The transparent indium-tin-oxide (ITO) electrodes are used in figure 64 (b)’s setup and the sample is observed in parallel direction. Both of the setup has an electrode gap of 125μm.
Figure 64 Custom-built apparatus for observing structure of VGCF in polymer matrix with optical microscope under electric field. (DC or AC) (courtesy of Tatshuhiro)

Figure 65 shows the experimental setup of magnetic field processing for the alignment of VGCF in UV-curable epoxy resin. The magnitude of permanent and superconductive magnets is 1T and 10T respectively.

Figure 65 A schematic procedure about magnetic processing of oriented VGCFs nanocomposite film (about 10μm thickness) based on UV-curable epoxy.

(courtesy of Tatshuhiro)

Therefore, it is promising and practical to develop such a protective “char” layer or nanocomposite that the CNTs or CNFs are intentionally oriented.
6.2.3. Modeling and theoretical work

While the experimental research methods provides a qualitatively concept of understanding the mechanisms of flame resistant of various types of systems, it is necessary to develop a mathematical model that is able to predict the development of flame propagation in a quantitative sense. However, it is extremely difficult to comprehensive model such a complex and unstable phenomena which involving the coupling of fluid dynamics, chemistry, and conjugate heat transfer between solid, liquid and gas phase. Nevertheless, it is still possible to make some relatively manageable models based on simplifying some conditions during combustion reaction. For example, the physical condition of combustion reaction is that the sample is horizontally exposed to a stable external heat flux and the materials in each phase are isotropic. When a simple model is set up, the condition can be extended in to filled polymer, filled composites and simple char-forming systems.

The ability to develop an accurate mathematical model to explain fire resistance mechanisms crucially depends on the understanding of fluid dynamics and degradation phenomenon of polymers. And also depends on the understanding of how these factors such as thermal conductivity, heat capacity, heat absorption of char, permeability of char, and viscosity of polymer affect the flammability of composites. Fortunately, the models to simulate the combustion phenomenon are abundant. [114][115]
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