A Dissertation

entitled

Kinetics and Mechanisms of the Oxidation Processes for

Unsaturated-Hydrocarbon-Modified Scavengers

by

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Poly(ethylene Terephthalate) (PET) is a prominent packaging material which is widely used in the plastic packaging industry. When compared with traditional packaging materials, such as steel and glass, the oxygen barrier property of PET is moderate at ambient temperature. The moderate oxygen barrier property of PET limits the application of PET for packaging some oxygen sensitive products, such as beer. Several approaches have been made to enhance “shelf life” of PET packaging material, especially for oxygen sensitive foods.

The active barrier packaging technique, which absorbs oxygen during its permeation route into packaged article, was studied in this research. Unsaturated hydrocarbons were used to modify PET to develop an oxygen scavenging system which can react with oxygen as an oxygen scavenger. In this research the unsaturated hydrocarbon is low molecular weight hydroxyl terminated polybutadiene. After the modification, the modified PET should maintain the favorable properties of PET and have an oxygen scavenging capability. The reason for blending hydroxyl terminated polybutadiene (HTPB) and PET was that the hydroxyl end group of HTPB was expected to react with end groups of PET to form a copolyester. The PET/HTPB copolyester will have different
optical, thermal and mechanical properties than those of a unreacted PET/PBD physical blend.

In this research, the oxidation mechanisms and kinetics of pure polybutadiene was studied first. Factors such as the molecular weight and composition of polybutadiene, which can affect oxidation mechanisms and kinetics, were analyzed. Activation energies of unsaturated olefin groups in the oxidation reactions were obtained. In the second portion of this research, low levels of hydroxyl terminated polybutadiene were reactively extruded with PET to form a polybutadiene modified PET. The oxidation kinetics and mechanism of this polybutadiene modified PET were also studied. Factors that can affect oxidation kinetics, such as the molecular weight of polybutadiene, concentration of polybutadiene, dispersion effect of polybutadiene in the modified PET and catalyst effect on oxidation kinetics, were included in the study of this unsaturated hydrocarbon modified PET.

The reactions between hydroxyl terminated polybutadiene and PET during the reactive extrusion process were also confirmed and identified by infrared end group analysis method, a proton NMR method and a content extraction method.

The evaluation of reactive extrusion process between polybutadiene and PET, were also studied. Finally suggestions were made on the future study of oxygen scavenging packaging techniques.
To my wife and parents for their endless love and support
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(d) 1049 cm\(^{-1}\) peroxyl group

(e) 1724 cm\(^{-1}\) carbonyl group  
(f) 3390 cm\(^{-1}\) hydroxyl group

Note:

(1) Relative peak area is measured peak area normalized to peak area of 1443 cm\(^{-1}\) methyl group.

(2) HTPB (Hydroxyl Terminated Polybutadiene): Mn=2800 g/mol, Mw=6200 g/mol, liquid

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(e) 1724 cm\(^{-1}\) carbonyl group  
(f) 3390 cm\(^{-1}\) hydroxyl group

Note:

(1) Relative peak area is measured peak area normalized to peak area of 1443 cm\(^{-1}\) methyl group.

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(e) 1724 cm\(^{-1}\) carbonyl group  
(f) 3390 cm\(^{-1}\) hydroxyl group

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(1) Relative peak area is measured peak area normalized to peak area of 1443 cm\(^{-1}\) methyl group.

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(e) 1724 cm\(^{-1}\) carbonyl group  
(f) 3390 cm\(^{-1}\) hydroxyl group

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Note:

(1) Relative peak area is measured peak area normalized to peak area of 1443 cm\(^{-1}\) methyl group.

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(e) 1724 cm\(^{-1}\) carbonyl group  (f) 3390 cm\(^{-1}\) hydroxyl group

Note:

(1) Relative peak area is measured peak area normalized to peak area of 1443 cm\(^{-1}\) methyl group.

(2) HTPB (Hydroxyl Terminated Polybutadiene): \(M_n=1200\) g/mol, 
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(a) 973 cm\(^{-1}\) Trans olefin group

(b) 1713 cm\(^{-1}\) Carbonyl group  (c) 3532 cm\(^{-1}\) Hydroxyl group.

Note: Relative peak area is measured peak area normalized to peak area of 1408 cm\(^{-1}\) methyl group

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Chapter 1

Introduction

1.1 Introduction to PET

Poly (ethylene Terephthalate) (PET) is a major synthetic polyester packaging material which is now widely used in the plastic packaging industry. PET was first introduced in 1941 when John Whinfield and James Dickson filed their patent for this fiber-forming polyester from the reaction of ethylene glycol with terephthalic acid. \[1\] PET has been utilized in the commercial market for various applications such as textiles, fibers, films, water and beverage containers and other food products.

In 2008 fifty million tons of PET resin were produced worldwide and this number keeps increasing by 4.6 percent annually \[2\] The growth of PET usage in the packaging industry, as a replacement for glass, metal and other plastics materials, has been extraordinary. PET is now a commodity polymer competing directly with polyethylene, polypropylene and styrene in the markets for food and beverage packaging.

PET has outstanding attributes including low manufacturing cost, ability to strain induced
crystallize, thermal resistance, clarity, high level of thermal and mechanical stabilities, good moldability and recyclability. The exceptional clarity of PET can increase the visual appeal of containers and the lightweight, high strength, moldability of PET containers make them a favorite with consumers. The dyeability of PET also increases the visual attraction of plastic packaging articles. The lightweight of PET containers also makes them easier to carry by consumers and decrease cost of storage and shipping by manufacturers. PET is also an environment friendly plastic which is easily recycled. All of these prominent properties originate from its chemical structure, as shown in Figure 1-1.

![Chemical structure of PET](image)

**Figure 1-1: Chemical structure of PET**

Generally the production of PET has two major approaches and different starting raw materials are used. One is the direct esterification of ethylene glycol (EG) with terephthalic acid (TPA) to produce bis(hydroxyethyl Terephthalate) (BHET) as monomer of PET. The other is transesterification between ethylene glycol (EG) and dimethyl terephthalate (DMT) produce bis(hydroxyethyl terephthalate) (BHET) as monomer of PET. BHET is polymerized by melt phase condensation reaction to produce PET.
Figure 1-2 shows the production of PET from ethylene glycol (EG) with terephthalic acid (TPA). Figure 1-3 shows the production of PET from ethylene glycol (EG) and dimethyl terephthalate (DMT).

1st step:

\[ \text{TPA} + 2 \text{HOCH}_2\text{CH}_2\text{OH} \rightarrow \text{BHET} + 2 \text{H}_2\text{O} \]

2nd step:

\[ n \text{HOCH}_2\text{CH}_2\text{O} \rightarrow \text{HOCH}_2\text{CH}_2\text{O} + n \text{EG} \]

Figure 1-2: PET syntheses from ethylene glycol (EG) with TPA
Common catalysts used in the production of PET include acetates of antimony (Sb), zinc (Zn) or lead (Pb), oxides of Sb, germanium (Ge), or Pb, Ti (OR) 4 and organotin compounds. Intrinsic viscosity (I.V.) is commonly used to describe the molecular weight of PET in industry. Intrinsic viscosity (I.V.) is one measurement of PET which depends on measurement conditions and solution system used. Different molecular weight levels of PET are used in various industrial applications. Higher molecular weight PET are typically produced by solid-state process polymerization (SSP) reaction under vacuum or in an inert gas atmosphere.
When compared with traditional packaging materials, such as steel and glass, the oxygen barrier property of PET is moderate at ambient temperature. The moderate oxygen barrier property of PET limits the application of PET for packaging some oxygen sensitive products, such as beer.\cite{6} The presence of high levels of oxygen in food packages may accelerate the spoilage of food and cause off-flavor and off-odor development, color changes, nutrient loss and microbial attack on the product. Control of the atmosphere inside the package therefore is critical to extend the food shelf-life.\cite{7,8,9}

The oxygen permeability of PET is relatively high when compared with some polymer materials. PET is a widely used commercial polymer material in packaging industry based on the cost, properties, processing and performance relationships. Efforts are continuing to reduce the oxygen permeability and enhance “shelf life” of PET packaging articles, especially for oxygen sensitive food packaging.
1.2 Introduction to Oxygen Scavenging Technique

In the food packaging industry, it is clear that oxygen plays a major role in the loss of food quality. High levels of oxygen present in the package contents will lead to food off-flavor, off-color and deterioration. Industries seek methods to reduce oxygen levels inside the package including using high oxygen barrier material to reduce oxygen permeation through packaging wall, vacuum packaging\(^{[10, 11]}\) and headspace removal\(^{[12, 13]}\) methods to reduce residual oxygen levels in the packaging process.

Two types of packaging techniques have been widely used in the packaging industry to achieve high oxygen barrier properties. One is the passive barrier packaging technique, which simply provides a high oxygen barrier to slow down oxygen permeation during the permeation process. The other is the active barrier packaging technique, which absorbs oxygen during its permeation route. Both of them can delay the adverse effect of the environment on the products in the containers. Figure 1-4 shows a comparison between a passive barrier technique and an active barrier technique.

A passive oxygen barrier system usually is a packaging wall with low oxygen permeability. The passive barrier can slow down the oxygen permeation process by decreasing oxygen diffusivity or solubility in the packaging wall. When a passive oxygen barrier system is applied, oxygen can be blocked outside the packaging wall so that only few of them can penetrate and the permeation speed is apparently decreased.
An active oxygen scavenging system will absorb oxygen during its permeation process through the packaging wall or absorb oxygen which is already sealed in the packaged article. The active oxygen scavenging system has the advantage over passive barrier techniques in that it can keep low levels of oxygen content inside packaged article by chemically reacting with oxygen whether it is residual oxygen inside packaging article or oxygen permeating through the packaging wall.

Figure 1-4: Schemes of passive barrier and active barrier techniques
1.3 Introduction to Unsaturated Hydrocarbon Modified PET

Incorporating an unsaturated hydrocarbon into PET provides an effective way to eliminate or at least control the amount oxygen diffusing through the PET bottle wall. Usually unsaturated hydrocarbon compounds or molecules contain a certain amount of unsaturated olefin which has high reactivity with oxygen. This kind of unsaturated hydrocarbon is usually referred to as an oxygen scavenger in the active barrier technique.

Before using unsaturated hydrocarbon to modify PET, other materials, such as iron powder, have been blended with PET as an oxygen scavenger. The main issue of blending solid face iron powder with PET is that the blend will lose the transparency of PET and be hard to recycle. When unsaturated hydrocarbon is incorporated into PET, usually this type of unsaturated hydrocarbon is used at low concentrations and has similar composition with PET, e.g. carbon and hydrogen atoms. As a result, a carefully designed organic oxygen scavenger modified PET will have comparable properties with virgin PET without sacrificing important properties of PET such as transparency, recyclability and high mechanical strength. The organic oxygen scavenger modified PET must meet several requirements as follow:

- Unsaturated hydrocarbon modified PET must have sufficient activity to react with oxygen, especially at room temperature.
The unsaturated hydrocarbon modified PET's properties cannot be changed too much, organic oxygen scavenger modified PET should be comparable with pure PET in terms of physical properties, such as strength, rigidity, clarity. If possible, transparent organic compounds modified PET is favored.

The unsaturated hydrocarbon modified PET should have the same or comparable recyclability as that of pure PET.

The cost of incorporating unsaturated hydrocarbon should be as low as possible.

The most commonly used unsaturated hydrocarbon is polybutadiene (PBD), which has high value of unsaturated olefin group. Incorporating PBD in the other polymer as been described in many patents.\cite{14,15} Unlike polymer blending system, such as polyethylene (PE)/ polybutadiene PBD or poly ethylene vinyl acetate (EVA)/ polybutadiene (PBD), PBD is not compatible with PET. The blending system of polybutadiene and PET should be modified in order to make PBD compatible with PET. One suggestion\cite{15} is to use hydroxyl terminated polybutadiene to react with PET during a reactive extrusion process. The hydroxyl end group of PBD will react with end groups of PET to form a copolyester molecule which has major sections of PET and a small amount of PBD. Because the PBD concentration in this PET/PBD blending system is low, the PET/PBD blend will have similar properties as PET. In this PET/PBD blending system, PET acts as a matrix and PBD acts as an active component. After modification, PET molecules still occupy the
majority of the PET/PBD blend and the blending system of PET and PBD will exhibit major properties of PET.
1.4 Oxidation Kinetics and Mechanism of Unsaturated Hydrocarbon Modified PET

Although unsaturated hydrocarbon modified PET as an oxygen scavenging system has been commercially available, the oxidation kinetics and mechanism of this system are still unavailable. Oxidation kinetics and mechanisms study of unsaturated hydrocarbon, such as oxidation mechanisms and kinetics of polybutadiene, has been studied since 1950’s. In the active scavenging system of PET and low molecule weight polybutadiene, however, the oxidation mechanism has not been verified and the oxidation kinetics of a blending system has not been studied.

Development of a PET/HTPB copolyester and study of its oxidation kinetics and mechanisms were the major aims of this thesis. Reaction routes and major oxidation reaction products were studied in this project. Factors that influence the oxidation reaction of oxygen scavengers in copolyesters, such as blends’ morphology, oxygen scavenger concentration and catalyst effect were also studied.
1.5 Objective

The major aims of this project were to study the extrusion blending process of oxygen scavenger and PET; verify the reactions between oxygen scavenger and PET, which was anticipated to generate a copolyester of oxygen scavenger modified PET; study the oxidation kinetics and mechanisms of the oxygen scavenger modified PET; and to evaluate the oxygen scavenger modified PET which was expected to exhibit similar properties as PET and much longer shelf life than PET.

Studying the oxidation mechanisms and kinetics of pure oxygen scavenger, such as polybutadiene, was the first objective of this project. Other researchers have shown that the oxidation reaction of polybutadiene is a first order reaction initiated by free radicals [75-79]. Experimental methods were developed to confirm the reaction route of the oxidation reaction of polybutadiene. Polybutadiene is a polymeric material whose molecular weight could affect its oxidation kinetics. Furthermore, polybutadiene has the three different olefin structures, cis, trans and vinyl. Different structures of three olefin groups in the polybutadiene may have different oxidation kinetics. Study of the oxidation behavior of pure oxygen scavenger will help further research on oxygen scavenger modified PET.

The second objective was to study the extrusion blending process of hydroxyl terminated polybutadiene and PET in which a copolyester of PET and hydroxyl terminated
polybutadiene was generated. During the melt blending (by twin-screw extrusions) process of HTPB and PET, reactions between the end groups of PET and the hydroxyl end group of HTPB were studied. Experimental method of verifying and studying reactions between PET and HTPB were developed. Factors that affect the reaction process between PET and HTPB, such as twin screw rotating speed, and residence time, were studied.

The third objective was to study oxidation kinetics of polybutadiene in PET/HTPB blends. In order to activate the oxidation reaction of polybutadiene in PET/HTPB blends at room temperature, catalyst was added to the blends. This portion of research was used to choose an optimum catalyst type and its concentration. Arrhenius equation parameters were obtained to study temperature dependence of oxidation kinetics of PET/HTPB blends. After the kinetic study, oxygen scavenging capacity and oxygen scavenging rate were determined.
Chapter 2

Literature Research

2.1 Oxygen Barrier Properties

Polyethylene terephthalate (PET) is a commercial packaging material which is widely used in the packaging industry. The low manufacturing cost, lightweight, extraordinary recyclability and aesthetic transparency of PET containers also makes them popular in food and beverage packaging industry. Extending shelf life of packaged item is a major consideration in the food and beverage packaging industry. Packaged food deterioration is a great concern in the food and beverage packaging industry. Most of the microorganisms in food deuteration are aerobic and consume oxygen. High levels of oxygen in the package may accelerate food spoilage, color and flavor alteration and microbiological attack. [16,17] Control of the oxygen existence level in the packaging article therefore is very critical. Lower oxygen levels in food and beverage packaging is desirable to enhance quality and safety of packaging items as well as to extent their shelf lives. Oxygen in the packaging article usually comes from two sources. These are residual oxygen sealed inside the packaging article during packaging process and oxygen
that permeates through the packaging wall after the packaging process. One method which is used to reduce residual oxygen levels during the packaging process is modified atmosphere packaging (MAP) \cite{18-22}, which use vacuum packaging\cite{19,20} or gas packaging \cite{21,22} techniques to change the gas atmosphere in the packaging process. To reduce the oxygen permeating through the package wall after the packaging process, high oxygen barrier materials are required.

Every polymer packaging material has its oxygen permeability according to its molecular structure, molecular weight and physical properties. Some packaging materials, such as ethylene-vinyl alcohol (EVOH) and Poly m-xylylenadipamide-nylon (MXD-6-nylon), have low oxygen permeability. The cost of EVOH and MXD-6, however, is much higher than that of commonly used food and beverage packaging materials, such as PET. Although PET is a prominent packaging material which is replacing high density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS) in packaging market\cite{23}, when compared with traditional material, e.g. steel and glass, the oxygen barrier properties of PET are only moderate at ambient temperature. Table 2-1 lists oxygen permeabilities of polymer packaging materials.
Table 2-1: Oxygen permeability data of selected polymers \[24\]

<table>
<thead>
<tr>
<th>Material</th>
<th>Permeability to Oxygen $\frac{\text{cm}^3 \cdot \text{mil}}{\text{day} \cdot 100\text{in}^2 \cdot \text{atm}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE (50% crystallinity)</td>
<td>480</td>
</tr>
<tr>
<td>Polyvinyl Fluoride</td>
<td>15</td>
</tr>
<tr>
<td>6,6 Nylon (20% crystallinity)</td>
<td>8</td>
</tr>
<tr>
<td>Polyvinyl Chloride (PVC)</td>
<td>8</td>
</tr>
<tr>
<td>Polyethylene Terephthalate (PET)</td>
<td>5</td>
</tr>
<tr>
<td>6,6,6 Nylon</td>
<td>1.5-2.5</td>
</tr>
<tr>
<td>Polyvinylidene Chloride (PVDC)</td>
<td>0.1</td>
</tr>
<tr>
<td>Polyacrylonitrile (PAN)</td>
<td>0.04</td>
</tr>
<tr>
<td>Polyvinyl Alcohol (PVA)</td>
<td>0.01</td>
</tr>
</tbody>
</table>
2.2 Passive Oxygen Barrier

In order to increase oxygen barrier properties and reduce residual oxygen levels in PET packages, two types of packaging techniques have been widely used in the packaging industry. One is the passive barrier packaging technique, which simply provides a high barrier to the outside environmental influences such as oxygen. The other is the active barrier packaging technique, which absorbs oxygen during its permeation route. Both of them can delay the adverse effect of the environment on the products in the containers.

A passive oxygen barrier technique is used to reduce oxygen permeability of packaging article by physical methods. Numerous passive barrier packaging technologies have been developed to enhance the barrier of PET to oxygen. For example, external or internal coatings for enhancing the gas barrier of PET containers have been developed. A surface coating can be applied to PET containers to improve oxygen barrier properties. The coating layer is normally a very high barrier layer, either inorganic or organic, and slows down the overall diffusion of oxygen. Coating techniques can be applied to monolayer PET container for their economies. BOC Coating Technology developed a silicon-oxide barrier coating layer, which is a clear and colorless silica coating layer with thickness of only 20-40 nanometers, for PET film. This technology can be applied in low temperature, plasma-enhanced chemical vapor deposition (PECVD) process. The silicon oxide layer can be bonded with PET material and increase the oxygen barrier property of
the container.

Sidel [26] developed an interior coating technique based on actis cold plasma technology which deposits a 100 nanometer thick hydrogenated amorphous carbon layer on the interior layer of a PET container. This coating technique can increase oxygen barrier property of a coated PET bottle by 30 times. PPG industries developed a Bairocade® coating system [27, 28] which can deposit epoxy-amine layer on the outside wall of a PET container. It is claimed that the shelf life of a Bairocade system coated PET bottle can be tripled and can make PET bottle possible for beer packaging. The coating technology, however, requires coating equipment not normally utilized in the manufacture of packaged beverages and therefore requires substantial capital investment and energy usage. In the packaging industries, high speed production [29, 30] of packaging containers will limit the usage of coating technique because of the complex design of high speed coating system.

Multi-layer packaging technique has been prevalent for several decades. Some other plastic materials, such as ethylene-vinyl alcohol (EVOH) and Poly (m-xylylenadipamide)-nylon, (MXD-6-nylon), have low oxygen permeability. The cost of EVOH and MXD-6 is much higher than that of commonly used polymer packaging material such as PET. Multilayer laminate structures of packaging container walls have also been used. In these structures, there are generally three to five layers in the packaging wall. Usually, the inner and outside wall is PET, and the center layer is a low
oxygen permeability EVOH\textsuperscript{[31-33]} or MXD-6\textsuperscript{[34-36]} film. Generally, high oxygen barrier polymer, e.g. EVOH, was co-extruded with PET to form multilayer structures. In the three layers design, the high oxygen barrier, such as EVOH, is sandwiched by PET structural layer. Mitsubishi Gas chemical\textsuperscript{[37, 38]} developed a three layer structure of PET bottle suitable for beer packaging. The inner and outer layer of this bottle is virgin PET; the middle layer is nanocomposite made of MXD6 nylon. It is claimed that the shelf life of this beer bottle can be extended to 110 days. The co-extrusion of multilayer packaging technique has higher productivity than coating technique. It is claimed that the multilayer PET bottle is more prevalent than coatings and accounts for 70\% of the barrier PET food packaging market. Coca-Cola Company\textsuperscript{[39]} also developed a five layers multilayer PET packaging system which has two layers of MXD6 which are sandwiched by three virgin PET or recycled PET layers. Although the oxygen barrier layer in the multilayer structure is thin, the cost of manufacturing will be elevated. Implementation of multilayer technology also requires substantial equipment investment, such as co-extrusion or multilayer injection molding equipments.\textsuperscript{[40-42]} The delaminating of the container layers made by this technique may impact appearance, barrier, and mechanical performance of the containers.\textsuperscript{[43, 44]} Furthermore, the multilayer structure may also impact the recyclability of homogeneous PET.\textsuperscript{[45, 46]}

When coating and multilayer technologies are compared, the coating technology requires less material cost but more equipment investment for complex high speed production line. The multilayer technology can meet the requirement of modern mass manufacturing but
with high equipment investment on co-extrusion or multilayer injection molding machines. Both of these two technologies attach high oxygen barrier layers onto or into PET bottle to increase overall oxygen barrier properties. One major benefit of PET material is the recyclability which helps PET dominating the food packaging market especially the beverage packaging area. Both coating and multilayer technology will encounter the elevated recycle cost of containers. [47]

Some attempts have been made to modify PET in order to enhance its oxygen barrier property. The common characteristics of these kinds of modifications are to optimize the physical behavior to reduce oxygen permeability. These modifications involve adding special oligomer or monomer onto the main PET chain by either copolymerization or transesterification during reactive extrusion. The aim of the added special oligomer or monomer is to increase polarity [48] by adding amide group, polarizability [49] by the addition of naphthalene group or increase the possibility of kink on the main chain [50] such as isophthalate group addition. These efforts can increase the barrier property of PET to some level; however, these modified PET materials still cannot reach the barrier property needed for high oxygen sensitive food packaging.

Another physical modification method is to improve oxygen barrier by change of crystallinity of PET container. PET is a semi-crystalline polymer. The strain induced crystallinity is an extraordinary character of PET which has the benefits of design flexibility and excellent mechanical strength. High levels of crystallinity, especially
orientation and strain-induced crystallization during the stretch–blow molding process, will give the PET bottle improved oxygen barrier property over unoriented, amorphous PET. [51-53] This physical modification method of PET to increase oxygen barrier is limited by the percentage of crystallinity of PET packaging material.


2.3 Active Oxygen Barrier

The development of active barrier packaging, which is a combination of oxygen barrier layers with oxygen scavenging, is among the leading packaging technologies for extension of shelf life. Several definitions exist in the literatures to characterize active packaging. Rooney\cite{12} defined active packaging as “packaging that performs a role other than an inert barrier to the outside environment”. Brody et al \cite{54} referred to active packaging as the packaging “intended to sense internal or external environmental change and to respond by changing its own properties or attributes and hence the internal package environment”. The main features of active packaging are to complement the deficiencies of the passive packaging by sensing and changing the packaging conditions to extend the shelf life of the inside contents. As Rooney\cite{55} pointed out later, two key features of active packaging are “removal of an unwanted component” and “addition of a desired ingredient”.

The first attempt of the packaging industry to develop active barrier containers was by adding a sachet inside the packaging structure as an oxygen scavenger. The sachet would contain a composition that reacts with oxygen. This type of oxygen scavenger was first developed by Japan’s Mitsubishi Gas Chemical Company during 1970s under the trade name Ageless \textsuperscript{®}\cite{56} as Figure 2-1 shows. This oxygen scavenger is an iron-based powder combined with a suitable catalyst. Mitsubishi Gas Chemical Company also developed
another oxygen scavenger for use as a sachet by using unsaturated fatty acid\cite{57}. Frandsen and his coworkers \cite{58} inserted a metal/polyamide complex into a sachet as an oxygen absorber. Pillsbury Corporation \cite{59} developed a pouch containing ascorbic acid as an oxygen scavenger. All these oxygen scavengers in sachet forms have good capabilities of absorbing oxygen in the package.

Figure 2-1: An example of Ageless® oxygen scavenger sachet

The addition of oxidizable sachets has several disadvantages. First, the addition of an oxidizable sachet requires additional packaging procedures \cite{56}. Second, some oxidizable compositions need adequate reaction conditions. For example, iron-based compositions need adequate moisture and low CO$_2$ contents to achieve optimized oxidation reaction rates. Finally, the most important disadvantage of the sachet technique is that the oxygen scavenging sachet will be put inside the packaging container and has a direct contact with food content as Figure 2-2 shows. As a result, the sachet technology has the danger that it may be accidentally ingested \cite{57}.
Blending an oxygen scavenger into PET to form an active oxygen barrier material is an approach in the effort to absorb oxygen diffusing into the PET material. If all the oxygen that diffuses into the PET material is consumed by the oxygen scavenger, the oxygen permeability of this new material is comparable with that of glass and steel. The oxygen scavengers can be categorized into two main kinds, inorganic and organic.

Some patents \cite{60-63} describe adding inorganic powders or salts directly into the PET packaging wall from which then can react with oxygen before it penetrates through the wall. The inventors proposed to add iron powder together with electrolytes such as metal halide, which would accelerate the iron oxidation reaction in the polymer matrix. The shortcomings of these approaches are the poor container clarity and the difficulty of dispersing the powder throughout PET material. Furthermore, the PET containing inorganic powders will have no recyclability advantage.

Incorporating organic oxygen scavenger into PET provides an effective way to eliminate
or at least control the amount of oxygen diffusing through the PET bottle wall. Several patents describe adding organic compounds into the polymer matrix as antioxidants. BP Amoco Corp.\[^{64}\] developed a copolymers system comprising polyester segments and polyolefin oligomer segments as oxygen scavengers to prolong shelf life. Cryovac Corp.\[^{65}\] developed a polymer oxygen scavenging system by incorporating oxidizable compounds (ethylenically unsaturated hydrocarbon) and transition metals as catalysts into the polymer matrix. Honeywell International Inc.\[^{66}\] introduced an oxidizable polydiene or oxidizable polyester into polyamide homopolymer as oxygen scavengers.

The incorporated organic oxygen scavenger is present in small amount and it has similar composition with that of PET, with respect to carbon and hydrogen atoms. As a result, a carefully designed organic oxygen scavenger modified PET will have comparable thermal and mechanical properties with virgin PET. The organic oxygen scavenger modified PET must meet several requirements as follow:

- It must have sufficient activity to react with oxygen, especially at room temperature.

- It should be comparable with pure PET in terms of physical properties, such as strength, rigidity, clarity.

- When an oxidation reaction occurs in the organic oxygen scavenger modified PET, severe decreasing of average molecular weight should be avoided. This means cleavage of PET main chain should be avoided.
- It should have the same or comparable recyclability as that of pure PET.

- The cost of incorporating organic compound into PET should be as low as possible.
2.4 Oxygen Scavenging Materials

There are several approaches for incorporating organic oxygen scavenger into PET to enhance oxygen barrier properties. The classic Oxbar® system \cite{67} is an example. In this case PET is blended with a certain amount of aromatic polyamide MXD-6 and metal catalyst through an extrusion process. With high temperature in the extrusion process, the ester group in PET and amide group in MXD-6 interchanges. \cite{98} Through this mechanism, some amount of MXD-6 segments with amide group transfer into the PET main chain and form a new polyesteramide molecule. The Oxbar® system has been demonstrated to be effective in reacting with oxygen, which reduces oxygen permeation to zero. The amide group which is easily attacked by the peroxyl intermediate in the oxidation reaction is transferred into the PET main chain. The main chain scission cannot be prevented. The main chain scission results in lower average molecular weight and a detectable clarity change.

Amosorb® technology \cite{68} developed by BP Amoco introduced incorporating polybutadiene into PET as an oxygen scavenger. According to the patent, PET with 4-12 wt% polybutadiene and certain amount of cobalt catalyst are blended through twin-screw extrusion. The PET and polybutadiene blend shows low oxygen permeability.

The reactions routes between PET and polybutadiene through extrusion have not been reported according to the published patent literature. Polybutadiene segments can be
incorporated into the PET main chain through the transesterification reaction between PET and polybutadiene molecules. There is also another possibility that polybutadiene molecule is incorporated into the end of PET molecule through functional end group reactions between end groups of PET and polybutadiene. If polybutadiene segments are incorporated into PET main chains, they can be easily broken by oxidation reactions, which will cause main chain scissions that will lower the average molecular weight. Incorporating polybutadiene segments onto PET molecules as chain ends or pendent groups may balance the requirement of increasing oxidation reactivity and avoiding main chain scission.

In the patent of Amosorb® technology the polybutadiene which is blended with PET could be either hydroxyl terminated or carboxyl terminated. The usage of functional terminating groups is to expect reactions between function groups of both PET and polybutadiene. No published literature has been found to confirm the reactions between functional terminated polybutadiene and PET during extrusion. Furthermore, although the patent of Amosorb® technology discloses that a PET and polybutadiene blend can be an effective oxygen scavenger, the oxidation reaction mechanisms and kinetics of PET and polybutadiene blends have not been reported. Since polybutadiene is a poly-olefin, which is believed to be oxidized in the PET/Polybutadiene blend, the inherent characteristics of polybutadiene itself and the interaction between PET and polybutadiene both can influence oxidation mechanisms and kinetics. The major aim of this research is
to study the reactions between PET and functional terminated polybutadiene and the oxidation mechanisms and kinetics of PET/polybutadiene blend.
2.5 Research Significance

Blending unsaturated hydrocarbons as oxygen scavengers with PET to extend shelf life of container contents is frequently studied in the plastic packaging industry. According to the present literature search, a blend system of polybutadiene and PET is the prevailing choice as an oxygen scavenging material. Challenges and opportunities both exist in this system and more research is needed.

For this research, a functional terminated polybutadiene was blended with PET by reactive extrusion to obtain an unsaturated hydrocarbon modified PET instead of a physical blend of polybutadiene and PET in this thesis. Reactions between functional end groups of polybutadiene and PET were confirmed and studied. Through the reactions between functional terminated polybutadiene and PET, a copolyester oxygen scavenging system was studied instead of the traditional physical blend of polybutadiene and PET. A hydroxyl terminated polybutadiene (HTPB) modified PET copolyester was expected to have different properties than a PET/polybutadiene (PB) physical blend system. The copolyester formed by the reactions between the end group of HTPB and the end groups of PET were studied. Using a copolyester system instead of a physical blend system has several benefits. Because the HTPB used in this thesis has lower molecular weight than the PET molecule and the oxygen scavenger concentration is low (0-5 wt %), the copolyester will have similar thermal and mechanical properties to those of PET.
Another benefit of this copolyester system is that the reactions between HTPB and PET can improve the distribution of the polybutadiene segments in the PET. Reactions between these two polymers will force HTPB to be distributed randomly in the PET, because of the random distribution of end groups of PET. The copolyester system will have better optical properties than a blend system. Normally, polybutadiene and PET are not compatible in the melt phase, which will generate phase separation in a PET/PB physical blend. A copolyester material which is generated from the two polymers can avoid severe phase separation, because the copolyester can act as a phase compatibilizer. The phase compatibilizer will prevent severe phase separation and thus improve optical properties of the blend.

Currently, no details of the oxidation mechanisms and kinetics of PET and polybutadiene blends have been discussed in the research literature. Mechanisms of the oxidation process of polybutadiene rubber, which is solid at room temperature have been studied for a long time.\textsuperscript{[40-42]} The oxidation process of polybutadiene is a self accelerated free radical reaction. For this thesis, extremely low molecular weight polybutadiene (1200 g/mol and 2800 g/mol), which is liquid at room temperature, were blended into PET material. The study of oxidation mechanism of low molecular weight polybutadiene in the liquid state and in the blend system is very important.

There are several possible factors that can affect oxidation kinetics of PET/PB blends. The molecular weight of polybutadiene, concentration of polybutadiene and morphology
of polybutadiene in PET/PB blends all can affect oxidation kinetics. The new copolyester based on hydroxyl terminated polybutadiene (HTPB) modified PET will also have different oxidation kinetics than PET/PB physical blends. All these factors were studied to develop a copolyester oxygen scavenging system, which can be oxidized at room temperature.

During the oxidation process, some oxidation products with small molecular weight may permeate through the packaging wall. Chain scission during oxidation will generate mechanical properties loss. In the PET/HTPB copolyester system, reactions between PET and HTPB could prevent severe chain scission. In this thesis, degree of transesterification reaction was studied at different melt extrusion operations conditions.
Chapter 3

Oxidation Mechanisms and Kinetics of Polybutadiene

3.1 Introduction

3.1.1 Polybutadiene materials

Polybutadiene is a synthetic polymer which is widely used in the manufacturing of tires, belt, hoses and toughened plastics. Polybutadiene has similar properties as natural rubber, so polybutadiene is always blended with other elastomers such as natural rubber for manufacturing tire treads and its sidewalls.

Polybutadiene is a homo-polymer which can be synthesized from 1-3 butadiene monomers. The polymerization process of polybutadiene was carried out in a reactor under controlled temperature, pressure and with catalyst. Catalysts that were used to polymerize polybutadiene include transition metal complexes such as neodymium, nickel, cobalt and alkyl metal such as butyllithium. The polymerization reaction of polybutadiene is commonly performed in solution system to avoid overheating because the reaction is an exothermic reaction, especially with butyllithium as catalyst. Figure 3-1 shows the polymerization path of polybutadiene form 1,3-butadiene monomer.
Figure 3-1: Polymerization of polybutadiene

In the polymerization process of polybutadiene utilization of different catalysts and
reaction temperatures and pressures will lead to different molecular configurations of
polybutadiene polymer. \(^{[70]}\)

Polybutadiene molecule has three molecular configurations of olefin groups which are cis-,
trans- and vinyl as Figure 3-2 shows. Polybutadiene polymers with different
concentrations of each configuration will have different physical properties. Polybutadiene
polymer with high cis- olefin concentration (>90%) will have higher cut growth resistance
and lower glass transition temperature. While, polybutadiene polymer with high trans-
olefin concentration (>90%) will have higher crystallinity.

Polybutadiene with high vinyl- olefin concentration will have higher cross-linking.

The polybutadiene polymer has large number of unsaturated olefin groups which can be
oxidized by oxygen. The three olefin configurations of polybutadiene will have different
stabilities and oxidation kinetics.
In chemistry, a reaction mechanism is the step by step sequence of elementary reactions by which overall chemical change occurs.\textsuperscript{(71)} A reaction mechanism describes reaction stages, reaction paths, reactants, reaction intermediates and reaction products. A well explained reaction mechanism can depict exactly what takes place at a certain stage of the reaction, which chemical bond is broken based on stereochemistry, what reaction product is formed at a certain stage of the reaction, and the relationships and orders of all involved reaction elements. In the realistic chemical world, however, only the net chemical change can be easily observed by monitoring reactants and reaction products. The instantaneous reaction intermediates and transition states are difficult to observe. Although in modern chemistry some experiments can be designed to mark reaction transition states or isolate some reaction intermediates, most reaction mechanisms are still suggestion models which lack
verifications by chemical methods. A well explained reaction mechanism is a predictive modeling which is consistent with experimental observations.

The study of oxidation mechanisms of polybutadiene started from the 1950’s and most literature [72-74] described the oxidation reaction of polybutadiene as a free radical reaction. A free radical reaction is a common reaction in organic chemistry and the common character of free radical reactions is the intermediate free radicals, which appear during the reaction and disappear later. The oxidation mechanisms of polybutadiene are described as following in the literatures as follows:

Olefin groups of the polybutadiene molecule combine with oxygen to form free radicals. Peroxyl and alkoxy free radicals are the major forms of free radical. Peroxide or hydroperoxide will be formed in the oxidation reaction as a reaction intermediate through a quick free-radical termination reaction. Because the free-radical formation and termination speed is assumed to be very high, once a peroxide or hydroperoxide intermediate appears, the oxidation reaction begins. The appearance time of peroxide or hydroperoxide can be considered as the oxidation induction time.

The alkoxy free radical can decompose into carbonyl [74], which is the final product of oxidation. At the final stage of oxidation reactions, all reaction intermediates, peroxide or hydroperoxide will convert into alkoxy free radicals and then decompose into carbonyl groups. Compounds with carbonyl groups are the final products of oxidation.
The olefin groups of polybutadiene have three configurations, cis, trans and vinyl structures. Generally, cis, trans and vinyl olefin groups are thought to have different reactivity in the oxidation reaction. In another words, these three olefin groups may or may not have the same reaction speed in free-radical formation and alkoxyl decomposition reaction. As a result, the percentages of cis, trans and vinyl olefin groups in the polybutadiene may have great effects on oxidation rates and product compositions.

Free radical reactions are chain reactions with a chain initiation step, a chain propagation step and a chain termination step.

**Step1: Chain initiation**

Figure 3-3 is the mechanism of chain initiation of polybutadiene oxidation.

![Figure 3-3: Free radical formation mechanism](image)

Figure 3-3: Free radical formation mechanism

Where

- RH: Polybutadiene Repeat Unit (one olefin double bond)
- R*(1): Un-conjugated alkyl free radical
R*(2): Conjugated alkyl free radical

ROO*: Peroxyl free radical

ROOH: Hydroperoxide

RO*: Alkoxyl free radical

With enough thermal agitation, a polybutadiene segment will convert from an un-conjugated structure to a more stable conjugated structure. During the transition from un-conjugated to conjugated structure, un-conjugated and conjugated alkyl free radicals are generated. Theoretically an un-conjugated alkyl free radical will change quickly into a more stable conjugated alkyl free radical. The conjugated alkyl free radical can combine with an oxygen molecule and a proton to form peroxide or hydroperoxide. Then the peroxide or hydroperoxide can decompose into peroxyl free radical and alkoxyl free radical.

Although the transition from un-conjugated to conjugated structure was already proven by other researchers, the un-conjugated and conjugated alkyl free radicals are only speculative and are hard to observe by current experimental methods. The final products of the free-radical formation reaction are two coexisting free radicals, peroxyl and alkoxyl free radicals.

The overall free-radical formation mechanism is:

\[ RH + O_2 \overset{k_1}{\rightarrow} ROO^* + H^+ \]  \hspace{1cm} (1)
In the free-radical formation process, oxygen is absorbed but the double bonds of olefin groups did not break. Furthermore, free radicals retain the configuration character: alkoxy and peroxy free radicals still can be distinguished as cis, trans and vinyl structures.

**Step2: Chain propagation**

Figure 3-4 is the mechanism of chain propagation of polybutadiene oxidation.

Figure 3-4: Chain propagation mechanism

The free-radical propagation step follows typical polymerization mechanism. In the Figure 3-4, ROO* is peroxy free radical and RO* is alkoxy free radical. When a free radical meets a polybutadiene segment, a double bond of that polybutadiene segment breaks to form a new covalent bond, accepts the free-radical molecule and forms a new
free radical. The result of chain propagation is cross-linking and molecular weight increase. Free-radical propagation does not consume oxygen but leads to the disappearance of double bonds.

\[ RO^* + RH \xrightarrow{k_3} R'O^* \] (3)
\[ ROO^* + RH \xrightarrow{k_4} R'O'O^* \] (4)

**Step 3: Chain termination**

When two free radicals collide, termination reactions between the free radicals will occur.

\[ RO^* + RO^* \xrightleftharpoons{K_5} ROOR \] (5)
\[ ROO^* + ROO^* \xrightleftharpoons{K_6} ROOR + O_2 \] (6)

The main product of the termination step is a peroxy crosslink or peroxide. The peroxy crosslink or peroxide can reversibly decompose into free radicals. The termination step does not consume olefin double bonds. The peroxide compound will decompose into oxidation final products through the β-scission reaction.

![β-scission of alkoxyl free-radical mechanism](image)

**Figure 3-5: β-scission of alkoxyl free-radical mechanism**
An alkoxyl free radical has low stability and can convert into carbonyl groups through the β-scission reaction.\textsuperscript{[73, 74]} Carbonyl-group formation and main-chain scission are the major results of β-scission reaction. From Figure 3-5, β-scission splits the covalent carbon-carbon bond between alkoxyl and olefin, and aldehydes are the major product of this scission. Aldehydes can be further oxidized into ketone, ester and carboxylic acid. All the products of β-scission reaction have the same characteristic, a carbonyl group. The β-scission reaction also leads to the disappearance of double bonds.

\[
RO^* + \frac{1}{2}O_2 \xrightarrow{k_7(\beta\text{-scission})} 2C = O
\]  \hspace{1cm} (7)
3.2 Experimental

3.2.1 Material

Two liquid polybutadiene materials purchased from Sigma-Aldrich Corporation were used in the oxidation experiments. Both of these polybutadiene materials were liquid at room temperature due to their low molecular weights. Table 3-1 lists the properties of two polybutadiene materials.

Table 3-1: Polybutadiene materials used in oxidation kinetics study

<table>
<thead>
<tr>
<th>Material</th>
<th>Properties</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Molecular weight Hydroxyl Terminated Polybutadiene (HTPB)</td>
<td>Average Mn=2800 g/mol</td>
<td>Very viscous colorless liquid</td>
</tr>
<tr>
<td></td>
<td>Average Mw=6200 g/mol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>D25°C=0.899 g/ml</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Viscosity: 48 poise(30°C)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10-25% Cis-1,4</td>
<td></td>
</tr>
<tr>
<td>Low Molecular weight Hydroxyl Terminated Polybutadiene (HTPB)</td>
<td>Average Mn=1200 g/mol</td>
<td>Viscous colorless liquid</td>
</tr>
<tr>
<td></td>
<td>Average Mw=2400 g/mol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>D25°C=0.913 g/ml</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Viscosity: 15 poise(30°C)</td>
<td></td>
</tr>
</tbody>
</table>

3.2.2 Methods

3.2.2.1 Methods of monitoring oxidation of polybutadiene

In order to monitor the oxidation reactions of polybutadiene, the oxidation reactant
(olefin group) lose rate, oxidation product (carbonyl) groups and oxidation intermediate (peroxide and hydroperoxide) groups need to be identified and quantified through a reliable experiment method. Common methods used to observe oxidation reaction of polybutadiene include NMR (nuclear magnetic resonance), FTIR (Fourier transform infrared spectroscopy) and ATR (attenuated total reflectance) technologies.

**NMR (Nuclear magnetic resonance)**

NMR (nuclear magnetic resonance) is a phenomenon which occurs when nuclei of certain atoms are immersed in a static magnetic field and exposed to a second electromagnetic pulse. Nuclei will absorb energy from electromagnetic pulse and radiate this energy. The energy radiating from nucleus in the NMR procedure is at specific frequency for a certain nuclei. This frequency can be used to observe specific quantum mechanical magnetic properties of an atomic nucleus. The frequency response of NMR phenomenon can be collected in NMR spectroscopy to exploit the magnetic properties of certain nucleus. The NMR phenomenon can be used to study the properties of material. The most common applications for NMR spectroscopy are proton NMR and carbon-13 NMR spectroscopy. Number and type of chemical entities in a molecule can be identified from NMR spectroscopy based on resonant frequency, energy of absorption and the intensity.

Organic molecules of a certain material, protons at different chemical environments (different locations in the molecule and different adjacent chemical bonds) will have
slightly different NMR resonance frequencies. An NMR resonance frequency can be divided by reference resonance frequency to its dimensionless number which is named as chemical shift. Thus, protons in the molecule will have different chemical shifts due to their chemical environment. Based on the information of chemical shifts, some structural information of a molecule can be obtained.

Figure 3-6 is a typical 400MHZ NMR spectrum of polybutadiene in a d-chloroform solvent. The doublet chemical shift appearing at (δ=5.43ppm,5.40ppm) represents protons of cis- or trans- olefin groups of polybutadiene. The doublet appearing at (δ=2.09ppm,2.04ppm) represents protons of the CH₂ methyl group of polybutadiene. Some small singlets (δ=1.30ppm, 1.45ppm, 4.32ppm, 4.80ppm, 5.57ppm) represent 1,2 butadiene groups (vinyl olefin) in the polybutadiene molecule. [82-84]
Figure 3-6: 400 MHZ Proton NMR Spectrum of hydroxyl terminated polybutadiene

(1200 g/mol)
NMR spectrum can provide detailed structural information of a molecule. For a polybutadiene molecule, however, NMR spectrum cannot easily distinguish Cis- and Trans- olefin structures.\textsuperscript{[83]} Chemical shift of Cis- olefin structure at 5.43 ppm and chemical shift of Trans- olefin structure at 5.40 ppm cannot be easily quantified because they are doublet. Protons on the cis- and trans- olefin groups have the exact same chemical environment but different structural configurations. Distinguishing different oxidation rates of cis- and trans- olefin groups is a key issue in the observation of oxidation reactions of polybutadiene. The second drawback of NMR is that in-situ scans of polybutadiene film sample are not available. Polybutadiene film sample has to be transferred into NMR tube to perform an NMR spectrum scan. The polybutadiene sample in the NMR test tube has low exposure to oxygen to conduct an oxidation experiment.

FTIR (Fourier transform infrared spectroscopy)

Fourier transform infrared spectroscopy is widely used in research and industry as a reliable technique for compound identification, quality control and in-situ monitoring of reactions.

Infrared spectroscopy (IR spectroscopy) studies the infrared region of electromagnetic absorption spectrum.\textsuperscript{[85-87]} The infrared region of the electromagnetic spectrum includes the near infrared region, mid infrared region and far infrared region. The mid infrared region is the most studied region for polymer materials. When an infrared light interacts with a sample material, chemical groups of this material will absorb infrared radiation in
a specific wave number. With this radiation energy, chemical groups of sample material will stretch, contract or bend at specific frequencies. The resonant frequencies and intensities can be used to identify chemical groups in the test sample. In addition, quantitative analysis in infrared spectroscopy can be applied to determinate the concentration of sample.

With development of many years, infrared spectroscopy techniques have been upgraded into the Fourier Transform Infrared (FTIR) spectroscopy from conventional dispersive infrared spectroscopy. FTIR is a measurement technique for collecting infrared spectra. Instead of recording the amount of energy absorbed when the frequency of the infra-red light is varied, the IR light is guided through an interferometer. Performing a mathematical Fourier transform on this signal results in a spectrum identical to that from the conventional infrared spectroscopy.

Since IR beam of FRIR machine penetrate the whole thickness of sample the FTIR theory follows the Beer-Lambert law [88-89] which is a linear relationship between absorbance and concentration of an absorbing species. The general Beer-Lambert law is usually written as:

\[ A = a(\lambda) * b * c \]

Here A is the measured absorbance, \( a(\lambda) \) is a wavelength-dependent absorptivity coefficient, b is the path length, and c is the concentration.

Experimental measurements are usually made in terms of transmittance (T), which is
defined as:

\[ T = \frac{I}{I_0} \]

Where \( I \) is the light intensity after it passes through the sample and \( I_0 \) is the initial light intensity. The relation between \( A \) and \( T \) is:

\[ A = -\log T = - \log \left( \frac{I}{I_0} \right) \]

In the Beer-Lambert law of FTIR theory, the absorptivity coefficient \( (a(\lambda)) \) and sample thickness can be calculated or measured for a certain sample. When absorptivity and sample thickness are known the concentration of certain compound in the sample can be calculated by the Beer-Lambert law.

**Attenuated total reflection (ATR)**

Attenuated total reflection (ATR) is a very useful technique for the study of the oxidation behavior of polybutadiene. For ATR, light is introduced into a suitable prism at an angle exceeding the critical angle for internal reflection producing an emission wave at the reflecting surface. \(^{90}\) When a sample contacts tightly with the prism, incident light will penetrate certain depth of the sample and reflect evanescent wave as Figure 3-7 shows. From the interaction of the evanescent wave with the sample, a spectrum can be recorded.
For polybutadiene, both Fourier transform infrared spectroscopy (FTIR) and attenuated total reflection (ATR) have the ability to distinguish cis, trans and vinyl isomers of olefin groups. ATR is obviously advantageous than FTIR transmission in monitoring oxidation process of low molecular weight polybutadiene. First of all, polybutadiene used in this project has typical weight average molecular weight of several thousand grams per mole, which is liquid in room temperature. ATR can easily measure infrared spectroscopy of both solid and liquid samples. For FTIR transmission spectrophy, casting a liquid film on the infrared transparent substrate is the traditional method. However, this method will not work in this project because the liquid polybutadiene will shrink or de-wet on the substrate surface during the oxidation which will devastate transmission depth constancy. Secondly, the FTIR transmission spectroscopy will involve oxygen diffusion factor in oxidation. Whereas ATR incident light only penetrate little thickness of the sample, where the penetrating thickness is related to incident light wavelength and refractive index difference between sample and prism. Generally, the penetrating thickness is only 2 to 5 micron in mid-infrared ATR spectroscopy. In this extreme thin layer, oxygen
diffusion factor can be neglected.

3.2.2.2 Experiment procedure

Liquid polybutadiene was transferred into aluminum pans with a diameter of 50 millimeters. High pressure nitrogen gas was blown on the liquid polybutadiene to help it spreading into a film on the surface of the aluminum pan. The transferred polybutadiene weight and density are calculated so as to spread the film with 100 micron thickness over the surface area of the pan. Then a group of aluminum pans was put into a forced-air-circulation oven to conduct the oxidation reaction. Each hour one aluminum pan was taken out of the forced air-circulation oven. Each aluminum pan with polybutadiene film on the surface was cut into 10 pieces and each film sample was flipped over, then the surface of the polybutadiene film was contacted with the ATR crystal machine to perform ATR spectrum scans. Spectra were acquired with an FTIR spectrometer (BOMEM MB155) using 4cm\(^{-1}\) resolution, 20 scans per minute in the 500cm\(^{-1}\) to 4000cm\(^{-1}\) range.

Both the high-molecular-weight HTPB and low-molecular-weight HTPB (Table 3-1) were oxidized at 55 ± 2°C from 0 to 20 hours, at 70 ± 1°C from 0 to 20 hours and at 100 ± 1°C from 0 to 10 hours.

During the oxidation test of liquid polybutadiene, the color of liquid polybutadiene gradually changed from transparent to yellow. After 10 days oxidation at 70°C, the liquid polybutadiene film changed into highly cross-linked solid film. Figure 3-8 displays ATR
spectra of each characteristic peak’s change with time from 0 to 20 hours during the 70°C oxidation.

Figure 3-8: High molecular weight HTPB (Mn=2800 g/mol) ATR spectra in 70°C oxidation.
Table 3-2 lists discernable peaks in the ATR spectra of high-molecular-weight HTPB oxidation reaction. For polybutadiene, 690 cm$^{-1}$, 1224 cm$^{-1}$ and 3004 cm$^{-1}$ peak correspond to cis- olefin group. Among these three peaks, 690 cm$^{-1}$ is influenced by noise from water and 1224 cm$^{-1}$ will be influenced by the oxidation product, therefore only the 3004 cm$^{-1}$ position can clearly represent the cis- olefin group. The 911 cm$^{-1}$ and 968 cm$^{-1}$ peak correspond to vinyl and trans- olefin groups, respectively.

The 1049 cm$^{-1}$ peak corresponds to the C-O stretching of C-O-O structure of peroxide or hydroperoxide. Both 1693 cm$^{-1}$ and 1724 cm$^{-1}$ represent carbonyl stretching features.

<table>
<thead>
<tr>
<th>Band (cm$^{-1}$)</th>
<th>Assign Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>690</td>
<td>Cis C=C deformation</td>
</tr>
<tr>
<td>911</td>
<td>CH=CH$_2$ out of phase deformation</td>
</tr>
<tr>
<td>968</td>
<td>Trans C=C deformation</td>
</tr>
<tr>
<td>1049</td>
<td>C-O of C-O-O- stretching</td>
</tr>
<tr>
<td>1180</td>
<td>C-O of O=C-O stretching</td>
</tr>
<tr>
<td>1224</td>
<td>Cis C=CH symmetric rock or C-O stretching</td>
</tr>
<tr>
<td>1443</td>
<td>CH3 asymmetric deformation</td>
</tr>
<tr>
<td>1639</td>
<td>C=O (cis and trans) stretching</td>
</tr>
<tr>
<td>1693</td>
<td>C=O of unsaturated (C=C-C=O-) stretching</td>
</tr>
<tr>
<td>1724</td>
<td>C=O of carbonyl group stretching</td>
</tr>
<tr>
<td>2858</td>
<td>C-H of CH2 group asymmetric stretching</td>
</tr>
<tr>
<td>2923</td>
<td>C-H of CH2 group symmetric stretching</td>
</tr>
<tr>
<td>3004</td>
<td>C-H of cis olefin group stretching</td>
</tr>
<tr>
<td>3070</td>
<td>C-H of terminal C=C stretching</td>
</tr>
<tr>
<td>3390</td>
<td>O-H stretching</td>
</tr>
</tbody>
</table>
The 3390 cm\(^{-1}\) peak corresponds to O-H stretch, which can be an alcohol group, hydroxyl segment of hydroperoxide or the hydroxyl segment of a carboxylic acid group. The 1639 cm\(^{-1}\) peak represents C=C stretching of an olefin double bond. The 2858 cm\(^{-1}\) and 2923 cm\(^{-1}\) peaks represent the methylene group in the polybutadiene. The 1443 cm\(^{-1}\) peak represents C-H deformation of CH\(_3\) methyl group.
3.3 Results and Discussions

3.3.1 Oxidation Mechanisms

Suggested oxidation mechanisms of polybutadiene were introduced in section 3.1.2 of this chapter. The suggested oxidation mechanisms are summarized as following:

Olefin groups of polybutadiene molecule will combine with oxygen to form free radicals. Peroxyl and alkoxyl free radicals are the major forms of free radicals. Peroxides or hydroperoxidse will be formed in the oxidation reactions as reaction intermediates through quick free-radical termination reactions. The alkoxyl free radicals will decompose into carbonyl group through β-scission reactions, which are the final products of oxidation.

3.3.1.1 Oxidation free radicals and intermediates

To confirm the oxidation mechanisms, high molecular weight polybutadiene (2800g/mol) was oxidized at 70°C in the forced-air-circulation oven to observe the whole oxidation process.

According to the suggested oxidation mechanism, the termination reaction of alkoxyl and peroxyl free radicals will generate peroxide or hydroperoxide. When oxidation proceeded to 12 hours, a 1049 cm⁻¹ peak can be seen in the Figure 3.8. The 1049 cm⁻¹ peak is the C-O stretching of C-O-O structure of peroxide or hydroperoxide. Peroxyl the free radical, peroxide or hydroperoxide all have the C-O segment. Because free radical is considered
as a transient intermediate with sparse content, the 1049 cm\(^{-1}\) peak can be attributed to a peroxide or hydroperoxide intermediate, which is the product of free-radical termination.

### 3.3.1.2 Oxidation process of polybutadiene

In order to clearly observe the oxidation process of polybutadiene, peak areas of vinyl-olefin groups, trans-olefin groups, cis-olefin groups, peroxyl groups, carbonyl groups and hydroxyl groups were calculated by peak calculation software. Figure 3-9 shows the peak area changes of major compounds in the 70°C oxidation reaction of high molecular weight polybutadiene.

The peak at 1443 cm\(^{-1}\) peak represents C-H deformation of CH\(_3\) methyl group. Methyl group is considered as an inert component in the oxidation reaction. Because the methyl group is considered stable and is not involved in the oxidation reaction, the 1443 cm\(^{-1}\) peak can be used as an internal-reference peak. To eliminate dispersion effect, every peak area is normalized to peak area of the 1443 cm\(^{-1}\) peak (methyl group).

The vertical coordinate of Figure 3-9 represents the relative peak area after normalization. Appendix 1 explained the peak normalization process.

In the oxidation reaction, the oxidation intermediate or products appear at a certain time which indicates that oxidation begins. This time is termed as oxidation induction time. In the polybutadiene oxidation, peroxide or hydroperoxide group (1049 cm\(^{-1}\)) as shown in Figure 3-9(d) is the oxidation intermediate and carbonyl group (1724 cm\(^{-1}\)) is the oxidation final product. In Figure 3-9, the 1049 cm\(^{-1}\) and 1724 cm\(^{-1}\) peak began to appear
at around 11 hours. As a result, the oxidation induction time is located roughly at 11
hours.

Figure 3-9: Relative peak area\(^{(1)}\) changes with time during HTPB\(^{(2)}\) oxidation at 70°C.
(a) 911 cm\(^{-1}\) vinyl olefin group  (b) 968 cm\(^{-1}\) trans olefin group
(c) 3004cm\(^{-1}\) cis olefin group  (d) 1049 cm\(^{-1}\) peroxyl group
(e) 1724 cm\(^{-1}\) carbonyl group  (f) 3390 cm\(^{-1}\) hydroxyl group

Note:
(1) Relative peak area is measured peak area normalized to peak area of 1443 cm\(^{-1}\) methyl group.
(2) HTPB (Hydroxyl Terminated Polybutadiene): \(M_n=2800\)g/mol, \(M_w=6200\)g/mol, liquid
Figure 3-9 shows that when oxidation began, vinyl- and trans- olefin groups began to decrease at 14 hours; cis- olefin group began to decrease at 6 hours; peroxide or hydroperoxide (1049cm\(^{-1}\)), which is reaction intermediate, appeared and kept increasing at 11 hours; carbonyl group (1724cm\(^{-1}\)), which is the oxidation final product, appeared and kept increasing at 11 hours; hydroxyl group(3390cm\(^{-1}\)) also began to increase at 11 hours, which indicates hydroxyl segment of hydroperoxide, alcohol or carboxylic acid also may be the product.

### 3.3.1.3 Oxidation products

In the suggested mechanism as Figure 3-5 shows, alkoxyl free-radical decomposition will generate the oxidation final product – carbonyl groups. Absorption bans at both 1693cm\(^{-1}\) and 1724 cm\(^{-1}\) represent carbonyl stretching features. Both of these peaks can be found in a certain stage of the test. 1693 cm\(^{-1}\) and 1724 cm\(^{-1}\) peak represent different kinds of carbonyl groups. The 1724 cm\(^{-1}\) peak represents the saturated carbonyl group, which is generated from the alkoxyl free radical losing olefin double bonds through a β-scission reaction. The 1693 cm\(^{-1}\) peak represents unsaturated carbonyl group.

The unsaturated carbonyl group structure is:

\[
\begin{align*}
\text{CH}_2 \text{CH} = \text{C} \text{H} \text{C} \text{O} \\
\text{CH}_2 \text{CH} = \text{C} \text{H} \text{C} \text{O}
\end{align*}
\]

A possible explanation of unsaturated carbonyl-group formation is suggested in path II of Figure 3-10, which indicates a different alkoxyl free-radical decomposition path instead
of β-scission reaction (Path I). In this alkoxyl free-radical decomposition (path II in Figure 3-10), the alkoxyl free-radical molecule loses a tertiary hydrogen and generates an unsaturated carbonyl group.

![Alkoxyl free-radical decomposition schemes](image)

From Figure 3-8, the appearance of two peaks, unsaturated (1693 cm\(^{-1}\)) and saturated (1724 cm\(^{-1}\)) carbonyl group, is very clear. The unsaturated carbonyl group (1693 cm\(^{-1}\)) appeared first at 12 hours and the size of this peak was tiny. When the oxidation proceeded to 15 hours, the saturated carbonyl group (1724 cm\(^{-1}\)) appeared gradually and the unsaturated carbonyl (1693 cm\(^{-1}\)) group kept diminishing. When the oxidation reaction proceeded to 20 hours, only saturated carbonyl group (1724 cm\(^{-1}\)) can be seen and the unsaturated carbonyl group (1693 cm\(^{-1}\)) had already disappeared. This phenomenon indicates that the unsaturated carbonyl group is not stable and can gradually convert into saturated carbonyl group. Because the 1693 cm\(^{-1}\) and 1724 cm\(^{-1}\) peaks are adjacent to each
other, there is no way to designate one as major peak and another as a shoulder. In the kinetic analysis, these two peaks are treated as one peak.

The 3390 cm\(^{-1}\) peak corresponds to O-H stretching, which can be an alcohol group, hydroxyl segment of hydroperoxide or the hydroxyl segment of a carboxylic acid group.

In Figure 3-9, it can be easily seen that the increase of hydroxyl group (3390 cm\(^{-1}\), O-H stretch) coincides with the increase of peroxyl group (1049 cm\(^{-1}\)). As a result, there is a possibility that the increase of hydroxyl group is due to the OH segment of hydroperoxide. Because of the very broad shape of the experimental O-H stretch peak and hydrogen bonding between hydroxyl groups, it is hard to differentiate the O-H group type. Generally, O-H stretch of alcohol group will appear at a relative higher wave number and O-H stretch of carboxylic acid group will appear at lower wave number.

Carboxylic acid, which is a possible final product, also has the O-H stretch peak. The carbonyl group (1724 cm\(^{-1}\)) peak formation coincides with 3390 cm\(^{-1}\) peak, also indicating the possibility of carboxylic acid.

The 1180 cm\(^{-1}\) peak corresponds to the C-O segment of an ester group, which indicates that an ester product exists in the system. Because a ketone only has the carbonyl group, it is hard to tell if a distinguishable ketone product exists or not in the system. As a result, ester, ketone and carboxylic acid can be considered as the final product of oxidation.
3.3.2 Oxidation Kinetics

The normal oxidation reaction of polybutadiene should follow a second order as:

\[
\text{[polybutadiene]} + \text{[O}_2\text{]} \rightarrow \text{[product]}
\]

The ATR technique only measures a very thin layer (2-5 micron) on the surface of the polybutadiene. In this extreme thin layer the oxygen diffusion restriction can be neglected and the oxygen concentration can be considered constant. Oxygen, one of the reactant, is present in such great amounts in this thin layer that its relative change will be too small, to be noticed during the reaction. The reaction then appears dependent on concentration of polybutadiene alone. The oxidation reaction of polybutadiene observed by the ATR technique can be treated as a pseudo-first-order reaction.

3.3.2.1 Oxidation Kinetics of High Molecular Weight Polybutadiene (Mn=2800 g/mol)

In the oxidation kinetic study of high molecular weight polybutadiene (2800 g/mol), characteristic peak areas of vinyl olefin group (911 cm\(^{-1}\)), trans olefin group (968 cm\(^{-1}\)), cis olefin group (3004 cm\(^{-1}\)), peroxide group (1049 cm\(^{-1}\)), carbonyl group (1724 cm\(^{-1}\)) and hydroxyl group (3390 cm\(^{-1}\)) were recorded through ATR spectrum. Figure 3-11, 3-12 and 3-13 display each characteristic peak’s changes with time during the HTPB 55°C, 70°C and 100°C oxidation respectively. To eliminate dispersion effect, every peak area is normalized to peak area of the 1443 cm\(^{-1}\) peak (methyl group asymmetric deformation). The vertical coordinate represents the relative peak area after normalization.
Figure 3-11: Relative peak area \(^{(1)}\) changes with time during HTPB \(^{(2)}\) oxidation at 55°C.

(a) 911 cm\(^{-1}\) vinyl olefin group  
(b) 968 cm\(^{-1}\) trans olefin group  
(c) 3004 cm\(^{-1}\) cis olefin group  
(d) 1049 cm\(^{-1}\) peroxyl group  
(e) 1724 cm\(^{-1}\) carbonyl group  
(f) 3390 cm\(^{-1}\) hydroxyl group

Note:

(1) Relative peak area is measured peak area normalized to peak area of 1443 cm\(^{-1}\) methyl group. 
(2) HTPB (Hydroxyl Terminated Polybutadiene): \(M_n=2800\) g/mol, \(M_w=6200\) g/mol, liquid
Figure 3-12: Relative peak area\(^{(1)}\) changes with time during HTPB\(^{(2)}\) oxidation at 70°C.
(a) 911 cm\(^{-1}\) vinyl olefin group   (b) 968 cm\(^{-1}\) trans olefin group
(c) 3004cm\(^{-1}\) cis olefin group   (d) 1049 cm\(^{-1}\) peroxyl group
(e) 1724 cm\(^{-1}\) carbonyl group   (f)  3390 cm\(^{-1}\) hydroxyl group

Note:
(1) Relative peak area is measured peak area normalized to peak area of 1443 cm\(^{-1}\) methyl group.
(2) HTPB (Hydroxyl Terminated Polybutadiene): \(M_n=2800\)g/mol, \(M_w=6200\)g/mol, liquid
Figure 3-13: Relative peak area\(^{(1)}\) changes with time during HTPB\(^{(2)}\) oxidation at 100°C.
(a) 911 cm\(^{-1}\) vinyl olefin group  (b) 968 cm\(^{-1}\) trans olefin group
(c) 3004 cm\(^{-1}\) cis olefin group  (d) 1049 cm\(^{-1}\) peroxyl group
(e) 1724 cm\(^{-1}\) carbonyl group  (f) 3390 cm\(^{-1}\) hydroxyl group

Note:
(1) Relative peak area is measured peak area normalized to peak area of 1443 cm\(^{-1}\) methyl group.
(2) HTPB (Hydroxyl Terminated Polybutadiene): \(M_n=2800\, \text{g/mol}, \, M_w=6200\, \text{g/mol}, \, \text{liquid}\)
Figure 3-11, Figure 3-12 and Figure 3-13 are Box and whisker plots. Each box in these three figures includes the statistical information of five summaries of experimental data which are the smallest observation (sample minimum), lower quartile, median, upper quartile and largest observation (sample maximum). The total statistical error of a measurement may come from oxidation reaction heterogeneity, experiment operation error and instrument limitations. The sample size of relative peak area measurement in these box plots is ten which means that ten polybutadiene oxidation samples were scanned by ATR in the experiments and represented as box in these box plots. From the lower quartile and upper quartile of each box in the Figure 3-11, Figure 3-12 and Figure 3-13 it can be observed that the statistical error level during the whole oxidation reaction changes with time. Standard deviations of carbonyl group (1724 cm$^{-1}$) measurements at different oxidation temperatures are listed in Figure 3.14 to illustrate the trend of statistical error level.
According to Figure 3-14, the first observation is that the standard deviation of relative peak area of carbonyl group during 55°C, 70°C and 100°C oxidation all increase with oxidation time. This result indicates that the oxidation reaction of polybutadiene film on the aluminum sample pan is not homogeneous. Because each polybutadiene film on the aluminum sample pan is cut into ten pieces to perform ten repeated ATR scans, the reaction degree on different locations of the film may be different. When oxidation reaction continues with time, the variance between different locations becomes bigger. The second observation also confirms the non-homogeneous oxidation reaction of polybutadiene film. With higher oxidation temperature, the standard deviation increases sharply. This result indicates that the variance between different locations on the polybutadiene film becomes bigger when the oxidation reaction is more severe. Standard
deviation calculations of other component of polybutadiene also confirm the observation that the oxidation reaction of polybutadiene is not homogeneous. The variance level increased with oxidation time especially at high temperature. Higher reaction rate or reaction degree will lead to high measurement variance.

The oxidation reaction of polybutadiene can be treated as pseudo-first-order reaction in the ATR spectra as previously described. A first-order reaction depends on the concentration of polybutadiene. Other reactants can be present, but each will be zero-order. The rate law for a first order reaction is:

\[ r = -\frac{d[A]}{dt} = kA \]

Where \( A \) is the concentration of reactant and \( k \) is the first order rate constant which has units of 1/time.

The integrated first-order rate law is:

\[ \ln[A] = -kt + \ln[A]_0 \]

A plot of \( \ln[A] \) vs. time \( t \) gives a straight line with a slope of \( -k \) which is reaction rate constant. In the pseudo-first order oxidation reactions of polybutadiene, the ATR spectra peak areas of each component group are treated as concentrations. The first-order rate law is transformed as:

\[ \ln \frac{[A]}{[A]_0} = -kt \]
Where \([A]\) is the observed relative peak area of ATR spectrum for each component in polybutadiene oxidation reaction and \([A]_0\) is the initial relative peak area of ATR spectrum for each component in polybutadiene before the oxidation reaction started.

Figures 3-1 to 3-17 represent each characteristic peak’s change of polybutadiene ATR spectrum with time during the HTPB 55°C, 70°C and 100°C oxidation respectively. The vertical axis is \(\ln \frac{[A]}{[A]_0}\), which is the left part of pseudo-first-order reaction rate law. And the slopes (k) in the figures are the first order reaction rate.
Figure 3-15: First order reaction rates for high M.W. HTPB in 55°C oxidation
(c) 911 cm\(^{-1}\) vinyl olefin group  (b) 968 cm\(^{-1}\) trans olefin group
(c) 3004 cm\(^{-1}\) cis olefin group  (d) 1049 cm\(^{-1}\) peroxyl group
(e) 1724 cm\(^{-1}\) carbonyl group  (f) 3390 cm\(^{-1}\) hydroxyl group
Figure 3-16: First order reaction rates for high M.W. HTPB in 70°C oxidation
(b) 911 cm\(^{-1}\) vinyl olefin group  (b) 968 cm\(^{-1}\) trans olefin group
(c) 3004 cm\(^{-1}\) cis olefin group  (d) 1049 cm\(^{-1}\) peroxyl group
(e) 1724 cm\(^{-1}\) carbonyl group  (f) 3390 cm\(^{-1}\) hydroxyl group
Figure 3-17: First order reaction rates for high M.W. HTPB in 100°C oxidation
(a) 911 cm\(^{-1}\) vinyl olefin group  (b) 968 cm\(^{-1}\) trans olefin group
(c) 3004 cm\(^{-1}\) cis olefin group  (d) 1049 cm\(^{-1}\) peroxyl group
(e) 1724 cm\(^{-1}\) carbonyl group  (f) 3390 cm\(^{-1}\) hydroxyl group
Figures 3-15 to 3-17 apply pseudo-first-order reaction rate law on the oxidation reactions of polybutadiene. In the oxidation reactants, vinyl-olefin group (911 cm\(^{-1}\)), trans-olefin group (968 cm\(^{-1}\)) and cis-olefin group (3004 cm\(^{-1}\)), the loss rates of reactants follow first order reaction rate law. In the oxidation intermediates and products, peroxyl group (1049 cm\(^{-1}\)), carbonyl group (1724 cm\(^{-1}\)) and hydroxyl group (3390 cm\(^{-1}\)), the formation rates also follow first order reaction rate law but some of them have two stages in the oxidation reaction. Figures 3-15 to 3-17 all indicate that the formation rates of oxidation intermediate, peroxyl group (1049 cm\(^{-1}\)), have two stages. The reaction rate of the first stage of peroxyl group formation is higher than the second stage of reaction. According to oxidation mechanisms of polybutadiene, the peroxyl group (1049 cm\(^{-1}\)) is oxidation intermediate, which is a transient product in the oxidation reaction of polybutadiene. With the oxidation reactions proceeding, the peroxyl groups (1049 cm\(^{-1}\)) will eventually convert into the final oxidation products. The formation rates of the peroxyl groups (1049 cm\(^{-1}\)) have two stages. This is reasonable because of the intermediate property of peroxyl group. Figures 3-16 and 3-17 indicate that the formation rates of carbonyl groups (1724 cm\(^{-1}\)) also have two stages. Carbonyl groups (1724 cm\(^{-1}\)) are groups of oxidation final products, such as ketones, esters, carboxylic acids and aldehydes, contains carbonyl (C=O) component. The composition and molecular weights of oxidation products which contain carbonyl groups are uncertain. There is a possibility that small molecular weight oxidation products can escape from sample film surface into the atmosphere. Losing
small molecular weight oxidation products into atmosphere will lead to observed oxidation formation rate decreases on the sample film surfaces. In the kinetics study of oxidation products, when formation rates of an oxidation product have two stages, only the formation rate of first stage is considered as real formation rate. The reaction rate constants for the oxidation reactants and products are given in Table 3-3. The activation energies calculated using the Arrhenius equation are given in Table 3-4.

Table 3-3: Oxidation rate constants of polybutadiene

<table>
<thead>
<tr>
<th>(per hour)</th>
<th>55°C</th>
<th>70°C</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1 ( vinyl olefin )</td>
<td>-0.0437</td>
<td>-0.0744</td>
<td>-0.0892</td>
</tr>
<tr>
<td>K2 ( trans olefin )</td>
<td>-0.0341</td>
<td>-0.0827</td>
<td>-0.1096</td>
</tr>
<tr>
<td>K3 ( cis-olefin )</td>
<td>-0.0202</td>
<td>-0.0686</td>
<td>-0.2886</td>
</tr>
<tr>
<td>K4’ (peroxyl group)</td>
<td>N/A</td>
<td>0.3065</td>
<td>3.9641</td>
</tr>
<tr>
<td>K4” (peroxyl group )</td>
<td>N/A</td>
<td>0.4269</td>
<td>0.1345</td>
</tr>
<tr>
<td>K5’ ( carbonyl group )</td>
<td>0.3640</td>
<td>0.8683</td>
<td>2.0094</td>
</tr>
<tr>
<td>K5” ( carbonyl group )</td>
<td>N/A</td>
<td>0.2757</td>
<td>0.1656</td>
</tr>
<tr>
<td>K6 ( hydroxyl group )</td>
<td>0.0594</td>
<td>0.3762</td>
<td>0.5955</td>
</tr>
</tbody>
</table>

Table 3-4: Activation energy in polybutadiene oxidation

<table>
<thead>
<tr>
<th>(per hour)</th>
<th>Activation energy (J/mol)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1 (vinyl olefin)</td>
<td>13909</td>
<td>0.8815</td>
</tr>
<tr>
<td>K2 (trans olefin)</td>
<td>22730</td>
<td>0.8724</td>
</tr>
<tr>
<td>K3 (cis-olefin)</td>
<td>53159</td>
<td>0.9292</td>
</tr>
<tr>
<td>K5’ (carbonyl group)</td>
<td>34004</td>
<td>0.9328</td>
</tr>
<tr>
<td>K6 (hydroxyl group)</td>
<td>44721</td>
<td>0.8417</td>
</tr>
</tbody>
</table>

From the calculated oxidation reaction activation energy values shown in Table 3-4, we can see that three olefin groups have different activation energies. Vinyl olefin has the lowest activation energy and highest oxidation rate, trans olefin group has the medium oxidation rate and cis olefin group has the lowest oxidation rate.
3.3.2.2 Oxidation Kinetics of low Molecular Weight Polybutadiene (Mn=1200 g/mol)

In order to compare the oxidation kinetics between polybutadiene materials with different molecular weight, a hydroxyl terminated polybutadiene which has 1200 gram per mole number average molecular weight was oxidized at 55°C, 70°C and higher temperatures. The characteristic peak areas of vinyl olefin group (911 cm\(^{-1}\)), trans olefin group (968 cm\(^{-1}\)), cis olefin group (3004 cm\(^{-1}\)), peroxide group (1049 cm\(^{-1}\)), carbonyl group (1724 cm\(^{-1}\)) and hydroxyl group (3390 cm\(^{-1}\)) were recorded through ATR spectrum. Figure 3-18 and 3-19 display each characteristic peak’s changes with time during the HTPB 55°C and 70°C oxidation respectively.
Figure 3-18: Relative peak area\(^{(1)}\) changes with time during HTPB\(^{(2)}\) oxidation at 55°C.

(a) 911 cm\(^{-1}\) vinyl olefin group  \(\rightarrow\) 968 cm\(^{-1}\) trans olefin group
(b) 968 cm\(^{-1}\) trans olefin group
(c) 3004 cm\(^{-1}\) cis olefin group  \(\rightarrow\) 1049 cm\(^{-1}\) peroxyl group
(d) 1049 cm\(^{-1}\) peroxyl group
(e) 1724 cm\(^{-1}\) carbonyl group  \(\rightarrow\) 3390 cm\(^{-1}\) hydroxyl group
(f) 3390 cm\(^{-1}\) hydroxyl group

Note:

(1) Relative peak area is measured peak area normalized to peak area of 1443 cm\(^{-1}\) methyl group.
(2) HTPB (Hydroxyl Terminated Polybutadiene): \(M_n=1200\) g/mol, \(M_w=2400\) g/mol, liquid
Figure 3-19: Relative peak area\(^{(1)}\) changes with time during HTPB\(^{(2)}\) oxidation at 70°C.

(a) 911 cm\(^{-1}\) vinyl olefin group  \hspace{1cm} (b) 968 cm\(^{-1}\) trans olefin group
(c) 3004 cm\(^{-1}\) cis olefin group  \hspace{1cm} (d) 1049 cm\(^{-1}\) peroxyl group
(e) 1724 cm\(^{-1}\) carbonyl group  \hspace{1cm} (f) 3390 cm\(^{-1}\) hydroxyl group

Note:

(1) Relative peak area is measured peak area normalized to peak area of 1443 cm\(^{-1}\) methyl group.
(2) HTPB (Hydroxyl Terminated Polybutadiene): \(M_n=1200\) g/mol, \(M_w=2400\) g/mol, liquid
As previously indicated, pseudo-first-order was applied on the oxidation kinetics of low molecular weight hydroxyl terminated polybutadiene (1200 g/mol). Reaction rates of vinyl olefin group (911 cm\(^{-1}\)), trans olefin group (968 cm\(^{-1}\)) and cis olefin group (3004 cm\(^{-1}\)) in low molecular weight HTPB (1200 g/mol) at 55\(^{\circ}\)C and 70\(^{\circ}\)C were calculated in Table 3-5 to be compared with reaction rates of high molecular weight HTPB (2800 g/mol).

Table 3-5: Oxidation rate comparison between two polybutadiene materials

<table>
<thead>
<tr>
<th>Olefin groups</th>
<th>Oxidation temperature</th>
<th>High M.W. HTPB Mn=2800 g/mol</th>
<th>Low M.W. HTPB Mn=1200 g/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl- olefin</td>
<td>70(^{\circ})C</td>
<td>-0.0744</td>
<td>-0.3471</td>
</tr>
<tr>
<td>Trans- olefin</td>
<td>70(^{\circ})C</td>
<td>-0.0827</td>
<td>-0.4534</td>
</tr>
<tr>
<td>Cis-olefin</td>
<td>70(^{\circ})C</td>
<td>-0.0686</td>
<td>-0.6442</td>
</tr>
<tr>
<td>Vinyl- olefin</td>
<td>55(^{\circ})C</td>
<td>-0.0437</td>
<td>-0.1508</td>
</tr>
<tr>
<td>Trans- olefin</td>
<td>55(^{\circ})C</td>
<td>-0.0341</td>
<td>-0.1004</td>
</tr>
<tr>
<td>Cis- olefin</td>
<td>55(^{\circ})C</td>
<td>-0.0202</td>
<td>-0.1218</td>
</tr>
</tbody>
</table>

It is clear that molecular weight of HTPB plays an important role on the oxidation kinetics of olefin groups. All the same oxidation temperature, oxidation reaction rates of olefin groups in a lower molecular weight HTPB are much higher than those in a higher molecular weight HTPB.

One or more oxidation temperatures higher than 70\(^{\circ}\)C should be tested for low molecular weight HTPB (1200 g/mol) to obtain activation energies of different olefin groups. Oxidation temperatures of 85\(^{\circ}\)C and 100\(^{\circ}\)C were also tested to oxidize low molecular weight polybutadiene. However, the data variances of FTIR spectrum peak calculation of
these two temperatures were unacceptable. In the 85°C oxidation of low molecular weight HTPB, huge data variance was found as Figure 3-20 shows.

Figure 3-20: Carboxyl group (1724 cm⁻¹) relative peak area scattering
Material: low molecular weight polybutadiene (Mₙ=1200 g/mol)
Oxidation temperature: 85°C

In the high-molecular-weight HTPB 100°C oxidation test, each sample at a given oxidation time is scanned at ten different locations. The error boxes of Figure 3-13 shows that each peak value has a little scatter after oxidation starts. After taking the average of five values, the curve can be trusted.

However, in the low-molecular-weight HTPB 85°C oxidation test, although each sample is still scanned at ten locations, the scatter of these ten peak-area values is large. Figure 3-20 shows scatter plot of carbonyl-group peak value versus time at 85°C. Apparently, because of the huge data scatter, ten values for each time point are not enough to take a
reliable average. As a result, the low molecular weight HTPB 85°C oxidation curve cannot be trusted.

These phenomena also indicate that HTPB oxidation is heterogeneous with location on the HTPB films. Several hours after commencing the oxidation, heterogeneity of reaction appears. With reaction proceeding, the heterogeneity becomes larger and larger (Figure 3-20). Certainly, oxidation rate may not be homogeneous in the polybutadiene, as disclosed by other researchers [96,97]. There is an expected competition between polymerization (crosslinking) and oxidation processes, and it may be that as local polymerization proceeds, the rapid rise in local viscosity inhibits the isomerization and oxidation processes. Note (Table 3-1) that initial viscosity of low-MW HTPB is much lower, so that relative viscosity changes would be much larger for that material as cross-linking form. Furthermore, with high oxidation rates, low molecule weight could be a possibility to generate high oxidation rate heterogeneity.

Low molecular weight HTPB (1200/g/mol) was also oxidized at 100°C to be compared with oxidation rates of high molecular weight polybutadiene (2800 g/mol). The experiment results show that the oxidation reaction of low molecular weight polybutadiene (1200 g/mol) is too fast to be scanned with ATR spectrum. When the oxidation reaction proceeds to 3 hours all low molecular weight polybutadiene sample film were already oxidized into highly-cross linked solids. The reaction is so fast that there is not enough time to perform ATR scan for these HTPB samples.
3.3.3 Proton NMR study of oxidation sequence of polybutadiene

In terms of the oxidation kinetic study of HTPB, the same olefin group of lower molecular weight polybutadiene has higher oxidation rates than that of the higher molecular weight polybutadiene. Proton NMR was used to study oxidation sequence of a polybutadiene molecule.

Figure 3-21: Software prediction of chemical shifts of unsaturated double bonds in a HTPB molecular chain

Figure 3-21 shows a software (ACD/Chemsketch 10.0) prediction of chemical shifts of unsaturated double bonds in a HTPB molecular chain. Protons of double bonds have different chemical shift due to their location. There are three locations of protons on double bonds:

5.78 ppm: C=C bonds at molecule end

5.57 ppm: C=C bonds near molecule end
5.40 ppm: C=C bonds in the middle of a polybutadiene molecule

The experimental NMR spectra were obtained by dissolving one drop of pure liquid HTPB (1200 g/mol) with D-chloroform in the proton NMR test tube. After obtaining NMR spectra, the NMR tube with HTPB was placed in the oven to perform oxidation tests at 70°C. Every 3 hours a proton NMR spectrum was obtained.

Figure 3-22: Proton NMR spectra of oxidation test of polybutadiene

Figure 3-22 clearly shows the oxidation result of pure polybutadiene. All intensities of three double bond protons begin to decrease due to the oxidation. Intensities of the three types of protons on the olefin double bonds during the 70°C oxidation are given in Table 3-6.
Table 3-6: Intensity changes of three protons on C=C during oxidation.

<table>
<thead>
<tr>
<th>Intensity</th>
<th>0 Hour</th>
<th>3 Hours</th>
<th>6 Hours</th>
<th>9 Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C 5.40 ppm</td>
<td>28.91</td>
<td>29.08</td>
<td>29.06</td>
<td>29.30</td>
</tr>
<tr>
<td>C=C 5.57 ppm</td>
<td>5.32</td>
<td>4.96</td>
<td>4.76</td>
<td>4.04</td>
</tr>
<tr>
<td>C=C 5.78 ppm</td>
<td>1.08</td>
<td>0.87</td>
<td>0.88</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Figure 3-23 gives graphical presentations of the data in Table 3-6. In the case of the three types of protons on the olefin double bonds of polybutadiene, protons at 5.40 ppm represent major protons on the olefin double bonds in the middle of polybutadiene molecular chain and protons at 5.57 ppm and 5.78 ppm represent very few olefin double bonds at or near the ends of the polybutadiene molecule. We can see that most of the chemical shift of C=C in polybutadiene molecules are located at 5.40 ppm. In the oxidation test from 0 hour to 9 hours, the intensity of 5.40 ppm did not decrease. Intensity at 5.57 ppm and 5.78 ppm decreases with oxidation time. This result indicates that olefin groups near or at the molecular ends of the polybutadiene molecule will be oxidized before those located in the middle position of the chain. The oxidation reaction of polybutadiene molecule is a free radical reaction. Different location of free radical on the polybutadiene may affect reactivities. Free radicals on the end of polybutadiene molecule were suspected to have higher reactivities than the other free radicals which located in the middle of polybutadiene molecule.
Figure 3-23: Intensity changes of three types of proton on C=C during oxidation

Olefin double bonds in the polybutadiene molecule will be oxidized sequentially by their locations. Olefin groups near or at molecule end will be oxidized first. Lower molecular weight polybutadiene will have more double bonds near or at molecular ends than the higher molecular weight polybutadiene has. As a result lower molecular weight polybutadiene will be oxidized faster than higher molecular weight polybutadiene.
Chapter 4

Oxidation Kinetics and Mechanisms of PET/Polybutadiene blends

4.1 Introduction

Blending unsaturated hydrocarbon as oxygen scavenger with PET to extend the shelf life of container contents is frequently studied in the plastic packaging industry. According to literature search, a blend system of polybutadiene and PET is a prevailing choice as an oxygen scavenging material.

As discussed in Chapter 3 low molecular weight liquid polybutadiene has been studied and proven to have very high oxidation kinetics. Currently, no details of the oxidation mechanisms and kinetics of PET and polybutadiene blends have been found in the literature. Mechanisms of the oxidation process of polybutadiene rubber which is a solid at room temperature have been studied for a long time \(^{[73,78]}\). The oxidation process of polybutadiene is a self accelerated free radical reaction. For this project, extremely low molecular weight hydroxyl terminated polybutadienes (1000 g/mol to 3000 g/mol), which are liquid at room temperature, were blended into PET material through the extrusion blending process. Reactions were expected between the end groups of HTPB and PET to
form a copolyester. The olefin double bonds of HTPB in the PET/HTPB blends were expected to react with oxygen and degrade to form oxidation products. Due to the matrix effect of PET, oxidation rate and oxidation induction times of polybutadiene in the PET/HTPB blends may be reduced to lower values than those of a pure polybutadiene.

There are several possible factors that can affect oxidation kinetics of PET/PB blends. The molecular weight of polybutadiene, concentration of polybutadiene and morphology of polybutadiene in PET/PB blends all can affect oxidation kinetics. The new copolyester based on hydroxyl terminated polybutadiene (HTPB) modified PET may also have different oxidation kinetics than PET/PB physical blends. The effect of catalyst in the oxidation kinetics of PET/THPB blends was also studied. All these factors were studied to understand an oxygen scavenging system based on PET/HTPB blend.
4.2 Oxidation Kinetics of PET/HTPB Blends

4.2.1 Experimental Materials

The liquid hydroxyl terminated polybutadiene materials purchased from Sigma-Aldrich Corporation were used in the oxidation experiments. Two kinds of hydroxyl terminated polybutadiene materials with different molecular weights were used in the blending process. These polybutadiene materials are liquid at room temperature due to their low molecular weights. The number average molecular weight of these two hydroxyl terminated polybutadiene is 1200 gram per mole and 2800 gram per mole.

The PET resin (Voridian Aqua PET WA314) used in this project is a commercial PET resin supplied by Eastman Chemical with an intrinsic viscosity of 0.72 dL/g.

4.2.2 Experimental Methods

Reactive Extrusion

A Werner & Pfleiderer (ZSK-30) co-rotating twin-screw extruder was used for reactive extrusion process. The temperatures of the five zones of the twin screw extruder were: zone 1 (270°C), zone 2 (270°C), zone 3 (270°C), zone 4 (270°C), zone 5 (270°C). The main screw speed was 300 rpm. The melting temperature of the die was 270°C. A vacuum pump was connected to zone 3 of the twin-screw extruder to evacuate volatile gas between resins. A nitrogen purge of 100 cc / min was applied to the extruder.

A liquid pump (Model CH-83) was used to inject liquid HTPB into the twin-screw
extruder. The liquid pump’s flow rate was carefully calibrated using two kinds of HTPB (see Appendix 2). Based on control settings of the PET resin feeding screw and the liquid pump, the HTPB concentrations in the PET/HTPB blends are 2 wt%, 4 wt% and 6 wt%.

The extruded HTPB/PET blends from the twin strand die were immediately quenched to roughly 15°C in quench water. Blend strands were pelletized through a Conair (Jetro Division) model 304 pelletizer. Blended pellets were dried at room temperature in vacuum oven for 24 hours and then sealed in plastic bags, thus avoiding or minimizing oxidation.

**Oxidation Test**

In preparation of analysis of oxidation of PET/HTPB blends using FTIR, five pellets of each blend with different HTPB types and concentrations were randomly chosen and pressed to films through a CARVER Laboratory Press machine with heating unit. Pellets were heated and kept at 200°F (93.3°C) under 5000 pounds pressure for 5 minutes and then freely cooled down to room temperature. The reason for this heating procedure is to remove internal stress in the film to prevent film shrinking under high temperature (The ATR cell with plate crystal requires a flat film). Film size pressed from pellet is approximately 5mm (length)×5mm (width) ×0.43mm (thickness) to facilitate handling. Films were stuck to aluminum bar as oxidation test specimen and every specimen was labeled. For each PET/HTPB blends material, 10 sample films were prepared.
Then films of PET/HTPB blends were put into a forced-air-circulation oven to conduct oxidation tests at 40°C, 55°C and 70°C. Each hour a sample film was taken out of the forced air-circulation oven to perform ATR spectrum scans. Spectra are acquired with an FTIR spectrometer (BOMEM MB155) using 4cm⁻¹ resolution, 20 scans in the 500cm⁻¹ to 4000cm⁻¹ range.

In the oxidation tests of pure liquid polybutadiene, the color of liquid polybutadiene changed from transparent to yellow. It was also observed that after 10 days of oxidation test at 70°C, liquid polybutadiene film changed into solid film which indicates cross linking occurred between polybutadiene molecules. In the oxidation test of PET/HTPB blend solid samples, the color of blend samples also changed from opaque white into yellow. The cross linking of polybutadiene during oxidation is a great concern for PET/HTPB blends. Because of the nature of cross linking material which is hard to be melt and hard to be dissolved in solvent, highly cross linked polybutadiene will devastate the recyclabiltiy of PET/HTPB blends. In the PET/HTPB blends, highly cross linked polybutadiene will also generate cavities in the solid blend. However, in the oxidation test of PET/HTPB blend, there is no cavities were observed except the color change.

4.2.3 Results and discussions of oxidation kinetics of PET/HTPB blends

The first step in the oxidation kinetics study is to find the locations of reactant including vinyl- olefin group, cis- olefin group and trans olefin group in the ATR spectrum of PET/HTPB blends. Due to low concentrations of HTPB in the PET/HTPB blends,
locating olefin double bonds of HTPB was a challenge. There are no new peaks in the blends, except a very tiny shoulder at the position of 2905 cm$^{-1}$. The tiny shoulder of 2905 cm$^{-1}$ peak is a C-H symmetric stretching of CH$_2$ group which is adjacent to C=C double bonds. Although the 2905 cm$^{-1}$ peak has relationship with olefin double bonds, the tiny shape and influence of adjacent peak prevent its use as a characteristic peak of olefin double bonds. All other infrared characteristic peaks of polybutadiene are overlapped by PET peaks.

A PET with 6 wt% HTPB blend sample was oxidized in the forced air oven and monitored by ATR spectra scans to find locations of the olefin groups. In a trial of oxidation study of HTPB/PET blends, the 973 cm$^{-1}$ peak was found to change during oxidation. The 973 cm$^{-1}$ peak is a trans- olefin peak in the oxidation kinetic research of pure liquid polybutadiene oxidation. However, in the locations of cis- olefin group and vinyl olefin group in the previous oxidation kinetics study, there were no trace of peak change found during this trial oxidation test. There is no cis olefin peak or vinyl olefin peak in PET/HTPB blends. According to our early study in oxidation mechanism research of pure liquid polybutadiene oxidation, the trans- olefin group is the most stable conformation of the three kinds of olefin groups. At high temperature, the cis- or vinyl olefin group will transform into trans- olefin group. At the high temperature (270°C) in the twin-screw extruder, all cis- or vinyl- olefin group are assumed to transform into trans- olefin groups.

Table 4-1 lists all the infrared peak definition in the PET/HTPB blend.
Table 4-1: ATR definition of peaks in PET/HTPB blend

<table>
<thead>
<tr>
<th>Wave number (cm(^{-1}))</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>723</td>
<td>(1) Ring C-H (2) O=C-O out of plane def</td>
</tr>
<tr>
<td>793</td>
<td>Ring C-H in plane def</td>
</tr>
<tr>
<td>845</td>
<td>CH(_2) Rocking Trans</td>
</tr>
<tr>
<td>872</td>
<td>Ring C-H out of plane def</td>
</tr>
<tr>
<td>899</td>
<td>CH(_2) Rocking Gauche</td>
</tr>
<tr>
<td>973</td>
<td>(1) Antisymmetric C-O STR Trans (2) Trans C=C</td>
</tr>
<tr>
<td>1016</td>
<td>Ring C-H in plane STR</td>
</tr>
<tr>
<td>1042</td>
<td>Antisymmetric glycol C-O STR gauche</td>
</tr>
<tr>
<td>1093</td>
<td>Symmetric C-O STR</td>
</tr>
<tr>
<td>1173</td>
<td>CH(_2) Twisting</td>
</tr>
<tr>
<td>1239</td>
<td>CH(_2) Twisting</td>
</tr>
<tr>
<td>1339</td>
<td>CH(_2) Wagging Trans</td>
</tr>
<tr>
<td>1370</td>
<td>CH(_2) wagging Gauche</td>
</tr>
<tr>
<td>1408</td>
<td>(1) CH(_2) bending (2) Ring C-H in plane Def</td>
</tr>
<tr>
<td>1451</td>
<td>CH(_2) Bending Gauche</td>
</tr>
<tr>
<td>1471</td>
<td>CH(_2) Bending Trans</td>
</tr>
<tr>
<td>1713</td>
<td>Carbonyl Group</td>
</tr>
<tr>
<td>2908</td>
<td>C-H symmetric stretching of CH(_2)</td>
</tr>
<tr>
<td>2956</td>
<td>C-H anti-symmetric stretching of CH(_2)</td>
</tr>
<tr>
<td>3532</td>
<td>O-H group</td>
</tr>
</tbody>
</table>

In the oxidation kinetic study of PET/HTPB (1200 g/mol) blends, characteristic peak areas of trans olefin group (973 cm\(^{-1}\)), carbonyl group (1713 cm\(^{-1}\)) and hydroxyl group (3532 cm\(^{-1}\)) were recorded through ATR spectrum. Figure 4-1, Figure 4-2 and Figure 4-3 display each characteristic peak’s changes with time when the PET/HTPB blends exposed to 70°C, 55°C and 40°C oxidation respectively. To eliminate dispersion effect, every peak area is normalized to peak area of the 1408 cm\(^{-1}\) peak (CH\(_2\) methyl bending in aromatic ring). The vertical coordinate represents the relative peak area after normalization. The calculation procedure of each ATR spectra of PET/HTPB blends was
introduced in Appendix-C.

Figure 4-1 displays trends of trans- olefin peak (971 cm\(^{-1}\)), carbonyl group peak (1713 cm\(^{-1}\)) and O-H group peak (3532 cm\(^{-1}\)) during 70\(^{\circ}\)C oxidation from 0 day to 15 days. In Figure 4-1 (a), the trans- olefin peak (971 cm\(^{-1}\)) decreases rapidly in the period of 0 to 3 days and reaches a steady plateau after 3 days. In Figure 4-1 (b), the carbonyl group peak (1713 cm\(^{-1}\)) increases rapidly in the period of 0 to 4 days reaching a maximum values and with increasing time, there is a slight decrease of the peak. In Figure 4-1 (c) the hydroxyl group peak (3532 cm\(^{-1}\)) has similar behavior to that of the carbonyl groups. In the period of 0 to 10 days, O-H group peaks increase; after 10 days oxidation, the peaks exhibit a decreasing tendency.

With all the information from Figure 4-1, oxidation reaction was mainly located in the period of 0 to 3 days. In this period, oxidation reactant (trans-olefin group) decreased and oxidation final product (carbonyl group) and hydroxyl group increased. After 3 days, the majority of the oxidation reaction was considered as completed. However, there comes a big concern of carbonyl groups. Carbonyl groups fluctuate and have a decreasing tendency from 3 days to 15 days. Almost all the blend films of different concentrations have this tendency. From oxidation reaction mechanism study of pure polybutadiene, it has been determined that the carbonyl group is the final product of oxidation. The lose rate of carbonyl group and hydroxyl only has one possibility: they are released into the atmosphere. HTPB has certain amounts of olefin double bonds in its molecules. Volatile small molecule will be generated when chain scission occurs between adjacent double
bonds. If volatile small molecules have carbonyl group and they are released into the atmosphere, the carbonyl group concentration of blend films will be diluted. Because ATR only measures an extremely thin layer on the film’s surface, whether small molecule release will happen inside the blend films is still questionable. In the later section of this chapter, a GC-MS test of released gas is performed to verify small molecules being released during oxidation.
Figure 4-1: Relative peak area change with time during PET/HTPB blends oxidation at 70°C
(a) 973 cm\(^{-1}\) Trans olefin group (b) 1713 cm\(^{-1}\) Carbonyl group (c) 3532 cm\(^{-1}\) Hydroxyl group.
Note: Relative peak area is measured peak area normalized to peak area of 1408 cm\(^{-1}\) methyl group.
Figure 4-2 displays trends of trans-olefin peak (971 cm\(^{-1}\)), carbonyl group peak (1713 cm\(^{-1}\)) and O-H group peak (3532 cm\(^{-1}\)) during 55°C oxidation from 0 day to 12 days. In Figure 4-2 (a), the trans-olefin peak (971 cm\(^{-1}\)) decreases rapidly in the period of 0 to 7 days and reaches a steady plateau after 7 days. In Figure 4.2 (b), in terms of the carbonyl group peak (1713 cm\(^{-1}\)) neither an increasing nor decreasing trend was found during the whole 12 days oxidation test period. The carbonyl groups keep fluctuating during the whole oxidation test period at 55°C. In Figure 4-2 (c) the hydroxyl groups (3532 cm\(^{-1}\)) have a steady increasing trend through the whole oxidation test period.

The oxidation reaction did happen during the 55°C oxidation test period of PET/HTPB blends which is verified by trends of trans-olefin groups and hydroxyl groups. The unavailable trend of carbonyl group in the 55°C oxidation test period also suggests that some carbonyl groups will be released into the atmosphere. When compared with behaviors of carbonyl groups in the 70°C oxidation test period, a rate competition between generating and releasing of carbonyl group is suspected in all oxidation tests. In the 70°C oxidation test, the carbonyl groups’ generation rates are higher than their releasing rate. As a result, carbonyl groups have an initial increasing trend; after the major oxidation is finished, carbonyl groups then have a decreasing trend. In the 55°C oxidation test period, the generation rate and releasing rate of carbonyl groups may be equal because of the lower reaction temperature. As a result, the carbonyl groups only have a fluctuating curve during 55°C oxidation test period. The average value of 1713 cm\(^{-1}\) peaks in Figure 4-2 (b) and Figure 4-5(b) has some difference. For PET/4wt%
HTPB blend and PET/6wt% HTPB blend, the average peak areas of 1713 cm\(^{-1}\) were around 9.5 and the average peak area of PET/2wt% was around 9.0. These results indicated that before the initial of oxidation, the blend sample had already been oxidized to different degrees. Although nitrogen purge had been applied to blow away residual air between PET resins during the twin screw extrusion of PET/HTPB blend, there still some oxygen was absorbed by PET resins before extrusion. With residual oxygen and the high temperature of extrusion, polybutadiene was easily oxidized to some extent during extrusion.
Figure 4-2: Relative peak area \(^{(1)}\) change with time during PET/HTPB blends oxidation at 55°C
(a) 973 cm\(^{-1}\) Trans olefin group (b) 1713 cm\(^{-1}\) Carbonyl group  (c) 3532 cm\(^{-1}\) Hydroxyl group.
Note: Relative peak area is measured peak area normalized to peak area of 1408 cm\(^{-1}\) methyl group.
Figure 4-3 displays trends of trans-olefin peak (971 cm$^{-1}$), carbonyl group peak (1713 cm$^{-1}$) and O-H group peak (3532 cm$^{-1}$) during 40°C oxidation from 0 day to 30 days. The first aim of this oxidation test is to examine the possibility of low temperature oxidation which is close to room temperature. Only the trans olefin group of PET/6 wt% HTPB blend has a obvious oxidation behavior which keeps decreasing from 8 days to 20 days. All the other oxidation products have no evidence of forming. In the oxidation kinetics study of PET/HTPB (1200 g/mol) blends, a 100°C oxidation test was also performed on the blend film samples. This attempt is to study the oxidation behavior of PET/HTPB blends at the temperature above glass transition temperature of PET. ATR spectrum scan of sample film requires a smooth and intimate contact between the surface of test film and ATR crystal. However, due to the internal force of PET/HTPB blend film and the high temperature, all sample films curled and deformed in the force-air oxidation oven. Other oxidation temperatures, such as 80°C and 90°C, were also tried. Curling and deformation cannot be avoided at oxidation temperatures higher than glass transition temperature of PET.
Figure 4-3: Relative peak area (1) change with time during PET/HTPB blends oxidation at 40°C
(a) 973 cm\(^{-1}\) Trans olefin group (b) 1713 cm\(^{-1}\) Carbonyl group (c) 3532 cm\(^{-1}\) Hydroxyl group.
Note: Relative peak area is measured peak area normalized to peak area of 1408 cm\(^{-1}\) methyl group.
In the previous oxidation mechanism study of pure polybutadiene, first order reaction rate law was successfully applied on the oxidation kinetics. In the kinetics study of PET/HTPB blends, a natural logarithm curve of peak area change is applied based on the first order reaction rate law. Slopes of natural logarithm curve are defined as reaction rates and units are per day. Table 4-2 lists the oxidation rate constants of PET/HTPB blends (2wt%, 4 wt% and 6wt%) during oxidation tests at different temperatures.

Table 4-2: Oxidation rate constants in the oxidation reaction of PET/HTPB blends

<table>
<thead>
<tr>
<th></th>
<th>HTPB concentrations</th>
<th>Trans- olefin group lose rate constant (per day)</th>
<th>Carbonyl group formation rate constant (per day)</th>
<th>Hydroxyl group formation rate constant (per day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70°C</td>
<td>2 wt% HTPB</td>
<td>-0.10</td>
<td>0.08</td>
<td>Not available</td>
</tr>
<tr>
<td></td>
<td>4 wt% HTPB</td>
<td>-0.13</td>
<td>0.12</td>
<td>Not available</td>
</tr>
<tr>
<td></td>
<td>6 wt% HTPB</td>
<td>-0.16</td>
<td>0.18</td>
<td>Not available</td>
</tr>
<tr>
<td>55°C</td>
<td>2 wt% HTPB</td>
<td>-0.047</td>
<td>Not available</td>
<td>0.072</td>
</tr>
<tr>
<td></td>
<td>4 wt% HTPB</td>
<td>-0.064</td>
<td>Not available</td>
<td>0.084</td>
</tr>
<tr>
<td></td>
<td>6 wt% HTPB</td>
<td>-0.085</td>
<td>Not available</td>
<td>0.088</td>
</tr>
<tr>
<td>40°C</td>
<td>2 wt% HTPB</td>
<td>Not available</td>
<td>Not available</td>
<td>Not available</td>
</tr>
<tr>
<td></td>
<td>4 wt% HTPB</td>
<td>Not available</td>
<td>Not available</td>
<td>Not available</td>
</tr>
<tr>
<td></td>
<td>6 wt% HTPB</td>
<td>-0.019</td>
<td>Not available</td>
<td>Not available</td>
</tr>
</tbody>
</table>

For the PET/6wt% HTPB blend, the activation energy of olefin group reaction is 63743 joule per mol based on Arrhenius equation calculations. For PET/2wt % HTPB blend and PET/4wt% HTPB blend, trans olefin group lose rate is only available at two temperatures, 70°C and 55°C. The calculation of activation energy of trans- olefin group will not be accurate although activation energy can be calculated by two reaction temperatures.

Reaction rates of polybutadiene in PET/HTPB blends are lower than the reaction rates of
polybutadiene in pure liquid state. For example, in the 70°C oxidation, the activation energy of trans-olefin group is 63743 joule per mole in a PET with 6 wt% HTPB blends; the activation energy of tran-olefin group rate in pure polybutadiene is 22730 joule per mole. The reaction speed of polybutadiene in solid state is obviously slower than that in liquid state. In a PET/HTPB blend, Oxidation rate may be influenced by matrix effect of PET. In the HTPB/PET blends, PET act as a matrix which will restrict oxidation reaction speed.
4.3 Factors affecting oxidation kinetics of PET/HTPB blends

4.3.1 HTPB concentration in the blends

In the oxidation kinetics study of PET/HTPB (1200g/mol) blends, three PET/HTPB blends with HTPB concentrations of 2wt%, 4wt% and 6wt% were tested at 40°C, 55°C and 70°C. Table 4-2 lists reaction rate constants of oxidation reaction of these PET/HTPB blends. From Table 4-2, a clear trend that can be seen is that at a certain oxidation temperature, higher HTPB concentration in the PET/HTPB blend will lead to higher reaction rates. Based on the oxidation kinetic data in Table 4-2, Figure 4-4 shows an increasing linear relationship between reaction rate constants and polybutadiene concentrations within the range tested in the blends.

Figure 4-4: Trans-olefin lose rate vs. HTPB concentrations in the PET/HTPB blends at 70°C oxidation
In common reaction kinetic calculations, initial reactant concentration is irrelevant with regard to reaction speed. In the PET/HTPB blends, matrix effect also plays an important role on the oxidation rate of polybutadiene. Matrix effects are the effects which cause changes in chemical or physical properties in any environment as compared to these quantities in a pure element. Pure polybutadiene has been observed to have high oxidation activities. When pure polybutadiene was blended into PET, oxidation rates of polybutadiene in the PET/HTPB blends were apparently lower than those of pure state. In the PET/HTPB blends, however, PET acts as the major matrix which limits the oxidation.

In the HTPB/PET blends, HTPB has additional effects on the blend matrix beyond being a reactant. In all HTPB/PET blends, higher HTPB concentration leads to higher oxidation rates. Oxidation rate may be determined by two factors. When PET and HTPB are blended through reactive extrusion, reactions will occur between them. In the PET/HTPB blend, certain amounts of the matrix are HTPB/PET copolyester, un-reacted PET and HTPB; When the HTPB concentration is higher, un-reacted HTPB in the blend could also act as a plasticizer which will reduce the matrix effect of PET. Higher HTPB concentration in the blends means lower PET concentration and weaker PET matrix effect. As a result, higher HTPB concentrations in the blends will lead to lower matrix effect which will enhance oxidation reaction speed.
4.3.2 Molecular weight of HTPB in the blends

In the previous oxidation kinetics study of pure polybutadiene, low molecular weight polybutadiene (1200 g/mol) exhibited higher oxidation rate than the higher molecular weight polybutadiene (2800 g/mol). Table 3-5 in Chapter 3 represents the comparison of oxidation rates between two pure polybutadiene materials with number average molecule weight of 1200 gram per mole and 2800 gram per mole respectively.

In the kinetics study of PET/HTPB reactive extrusion blends, a comparison of oxidation rates between two PET/HTPB blends with different molecular weight HTPB was also performed. The experimental parameters of twin-screw reactive extrusion were exactly same except a high molecular weight polybutadiene with number average molecular weight of 2800 gram per mole HTPB was used in the blend with Voridian Aqua PET WA314. Based on control setting of PET resin feeding screw and liquid pump, the high M.W. HTPB concentrations in the PET/HTPB blends are 2 wt%, 4wt% and 6wt%. After reactive twin-screw extrusion, extruded pellets of PET/HTPB blends were pressed into films to be oxidized at 70°C. In the oxidation kinetic study of PET/HTPB (2800 g/mol) blends, characteristic peak areas of trans olefin group (973 cm\(^{-1}\)), carbonyl group (1713 cm\(^{-1}\)) and hydroxyl group (3532 cm\(^{-1}\)) were recorded through ATR spectrum. Figure 4-5 displays each characteristic peak’s changes with time during exposure of the PET/HTPB(2800 g/mol) blends to 70°C oxidation.
Figure 4-5: Peak area changes during oxidation test of high M.W. HTPB and PET blends at 70°C
(a) 973 cm\(^{-1}\) Trans olefin group
(b) 1713 cm\(^{-1}\) Carbonyl group
(c) 3532 cm\(^{-1}\) Hydroxyl group
Figure 4-3 displays trends of trans-olefin peak (971 cm$^{-1}$), carbonyl group peak (1713 cm$^{-1}$) and O-H group peak (3532 cm$^{-1}$) during 70°C oxidation from 0 day to 12 days. In Figure 4-3 (a), the trans-olefin peaks (971 cm$^{-1}$) of PET/4wt% HTPB (2800 g/mol) and PET/4wt% HTPB (2800 g/mol) have clear oxidation characters. Blend sample of PET/2 wt% in Figure 4-3 (a) had no obvious oxidation behavior. In Figure 4-2 (b) and Figure 4-2 (c), the carbonyl group peak (1713 cm$^{-1}$) and hydroxyl groups (3532 cm$^{-1}$) of all blends sample keep fluctuating during the whole oxidation test period.

With the pseudo-first order reaction rate law, the kinetics study of PET/HTPB blends is applied with a natural logarithm conversion (see Appendix 3 for details). Slopes of natural logarithm curve are defined as reaction rates and unit is per day. Table 4-3 lists the trans-olefin oxidation rate constants of PET/high M.W. HTPB blends (2wt%, 4 wt% and 6wt%) during oxidation tests at different temperatures. Table 4-3 also lists trans-olefin oxidation rate constants of PET/low M.W. HTPB blends which were obtained previously to be compared with oxidation rate constants of PET/high M.W. HTPB blends.
Table 4-3: Comparison of oxidation reaction constants of PET/low M.W. HTPB blends and PET/high molecular weight HTPB blends in the 70°C oxidation test period

<table>
<thead>
<tr>
<th></th>
<th>HTPB concentrations</th>
<th>Trans- olefin group lose rate constant (per day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET/ low M.W. HTPB</td>
<td></td>
<td></td>
</tr>
<tr>
<td>blends (1200 g/mol)</td>
<td>2 wt% HTPB</td>
<td>-0.10</td>
</tr>
<tr>
<td></td>
<td>4 wt% HTPB</td>
<td>-0.13</td>
</tr>
<tr>
<td></td>
<td>6 wt% HTPB</td>
<td>-0.16</td>
</tr>
<tr>
<td>PET/ High M.W. HTPB</td>
<td></td>
<td></td>
</tr>
<tr>
<td>blends (2800 g/mol)</td>
<td>2 wt% HTPB</td>
<td>unavailable</td>
</tr>
<tr>
<td></td>
<td>4 wt% HTPB</td>
<td>-0.037</td>
</tr>
<tr>
<td></td>
<td>6 wt% HTPB</td>
<td>-0.046</td>
</tr>
</tbody>
</table>

Although the trans-olefin reaction rate constant of PET/high M.W. HTPB blend is unavailable during the 70°C oxidation test, a conclusion still can be drawn that PET/high M.W. HTPB blend has much lower oxidation rate than PET/low M.W. HTPB blend sample. For example, the reaction rate of low molecular weight HTPB in the PET/6 wt% HTPB blend is 3.48 times faster than the reaction rate of high molecular weight HTPB in the blends with the same concentration. This observation agrees with the previous oxidation kinetics study of pure liquid polybutadiene. In both case the low molecular weight polybutadiene has higher oxidation kinetics than that of a high molecular weight polybutadiene.
4.3.3 Dispersion of HTPB in the PET/HTPB blends

The dispersion effect of HTPB in PET/HTPB blends is also suspected to affect the oxidation kinetics of the blends. Morphology studies of PET/HTPB blend by Fei,Xie\textsuperscript{[98]} shows that HTPB and PET are two immiscible polymers. Phase separation occurs in PET/HTPB blends which causes reduced clarity of film made from the blends. Polybutadiene tends to agglomerate to small particles in PET/HTPB blends. Figure 4-6 assumes a scenario in which two PET/HTPB blend samples which have the same amount HTPB inside are exposed to oxygen. It is clear that the polybutadiene which disperses into smaller particles will have higher surface area to contact oxygen. Good dispersion of HTPB in PET/HTPB can be expected to enhance oxidation kinetics.

Figure 4-6: A scenario that two PET/HTPB blend samples which has same amount HTPB inside are exposed to oxygen
In reactive twin-screw extrusion of PET/HTPB blends, main screw speed can affect dispersion effect of HTPB in the blend. Mechanical torque of the screw will break HTPB liquid into small particles. Higher screw rotating speed will have better dispersion effect on the HTPB in the blend.

Three PET (HP 806, 0.84 I.V.)/HTPB (2,800 g/mol) blends with 5 wt% HTPB were extruded by twin screw extruder. Three twin screw rotating speeds (200 rpm, 300 rpm, 400 rpm) were used. Oxidation kinetics of the three samples was studied at two temperatures (55°C and 70°C). Extrusion temperatures were 270°C for all heating zones of twin-screw extruder.

Figure 4-7 shows changes of trans-olefin group (973 cm\(^{-1}\)) during 70°C oxidation from 0 hours to 92 hours. Figure 4-8 shows changes of trans-olefin group (973 cm\(^{-1}\)) during 55°C oxidation from 0 hours to 240 hours. The decreasing curve of trans-olefin group (973 cm\(^{-1}\)) was considered as a first order reaction and natural logarithm conversion was applied. Rate constants of decreasing of trans-olefin group (973 cm\(^{-1}\)) were calculated as shown in Table 4-4.
Figure 4-7: Trans C=C olefin group in 70°C oxidation test

Figure 4-8: Trans C=C olefin group in 55°C oxidation test
Table 4-4: Oxidation rate constants for PET/HTPB blends with different extrusion twin screw rotating speeds at 70°C and 55°C

<table>
<thead>
<tr>
<th>Screw (rpm)</th>
<th>Oxidation temperature (°C)</th>
<th>Trans-olefin decreasing rate (per hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>70</td>
<td>-0.00110</td>
</tr>
<tr>
<td>300</td>
<td>70</td>
<td>-0.00199</td>
</tr>
<tr>
<td>400</td>
<td>70</td>
<td>-0.00189</td>
</tr>
<tr>
<td>200</td>
<td>55</td>
<td>-0.00078</td>
</tr>
<tr>
<td>300</td>
<td>55</td>
<td>-0.00144</td>
</tr>
<tr>
<td>400</td>
<td>55</td>
<td>-0.00134</td>
</tr>
</tbody>
</table>

From trans-olefin group decreasing rate in Table 4-4, it can be clearly seen that higher screw rotating speed will lead to higher oxidation rate. The reaction rate constants in the 200 rpm screw rotating speed condition is obviously lower than those in the 300 rpm and 400 rpm screw rotating speed condition. There is no obvious reaction rate difference of 300 rpm and 400 rpm screw rotating speeds. These experiment results indicate that high twin screw rotating speed will reduce particle size of HTPB in PET/HTPB blend and increase oxidation rate and 300 rpm screw rotating speed is enough to break polybutadiene into small particles.

In the Figure 4-7 which represents trans-olefin group lose rates in the 70°C oxidation of PET/HTPB blends, there can be seen increasing trans-olefin groups from 0 hours to 16 hours for all samples. After oxidation time at 16 hours, all trans-olefin groups began to decrease with oxidation reaction proceeding. Similarly, in the Figure 4-8 which represents trans-olefin group lose rates in the 55°C oxidation of PET/HTPB blends, there can be seen an increasing trans-olefin from 0 to 40 hours for 200 rpm sample; from 0 to 20 hours for 300 rpm sample and from 0 to 60 hours for 400 rpm sample. After all
trans-olefin groups reached their maximum value they began to decrease with oxidation reaction proceeding. In the calculation of oxidation rates of trans-olefin groups, these increasing trends of trans-olefin groups were not considered. The beginning of the oxidation reactions of trans-olefin groups were considered as they reached maximum value.

In the analysis of unexpected initial increasing trend of trans-olefin group in the oxidation reactions of PET/HTPB with different twin-screw rotating speeds, data variance was suspected to cause the initial increasing trend. Figure 4-9 is box and whisker plots of trans-olefin groups in the 70°C and 55°C oxidation tests of PET/HTPB blends with different twin-screw rotating speeds. Each box in the figure includes the statistical information of smallest observation (sample minimum), lower quartile, median, upper quartile and largest observation (sample maximum). The sample size of relative peak areas measurement in these box plots is nine which means that nine PET/HTPB blend oxidation samples were scanned by ATR in the experiments and represented as box in these box plots. Figure 4-9(a), (b) and (c) represent change of relative peak areas of trans-olefin groups in the 70°C oxidation of PET/HTPB blends with different twin-screw rotating speeds. From the boxes in Figure 4-9(a), (b) and (c), it is clear that the relative peak area variances in the initial increasing trends (before 20 hours) are larger than those in the latter decreasing trends (after 20 hours). Figure 4-9(d), (e) and (f) represent change of relative peak areas of trans-olefin groups in the 55°C oxidation of PET/HTPB blends with different twin-screw rotating speeds. Boxes in the Figure 4-9(d) and (f) also
show that variances of olefin group relative peak areas in the beginning increasing trend are larger than those in the latter decreasing trends. To quantify variances in the oxidation reaction of PET/HTPB blends with different twin-screw rotating speeds, standard deviations of each box in the Figure 4-9 were calculated.

Figure 4-10 shows the average standard deviations in the initial increasing relative peak areas of olefin group and the later decreasing relative peak areas. For the oxidation reaction at 70°C, two average standard deviations were calculated for each PET/HTPB sample. One is the average of standard deviations of initial increasing olefin groups before 16 hours and the other is the average of standard deviations of decreasing olefin groups after 16 hours. For the oxidation reaction at 55°C, average standard deviations are calculated for the relative peak areas before and after 40 hours for PET/HTPB blends with 200 rpm twin-screw rotating speed; for the relative peak areas before and after 20 hours for PET/HTPB blends with 300 rpm twin-screw rotating speed; for the relative peak areas before and after 60 hours for PET/HTPB with 400 rpm twin-screw rotating speed.

In the Figure 4-10(a) and (b) which compare the average standard deviations of olefin groups relative peak areas between initial increasing trend and later decreasing trend, all the standard deviations of initial increasing trend is much larger than those of the later decreasing trend. This phenomenon indicates that the initial increasing trend of olefin group before oxidation started is at unstable condition. Before the olefin groups starts to decrease in the oxidation, there exhibits huge variances of relative peak areas of olefin
group in the PET/HTPB blend samples. Because changing twin-screw rotating speeds in the blending process of PET and HTPB, the pressure, twin-screw rotating torque and residence time of materials are different. As a result the distributions of HTPB in the PET/HTPB blends are not the same due to different twin-screw rotating speeds. In the initial time period of oxidation test, the HTPB molecules may start migrating or stabilizing themselves in the PET/HTPB blends when exposed to higher temperature. This stabilization process of HTPB molecules may be the reason of initial increasing trend of olefin groups and their huge variance before oxidation starts. The second observations is that the standard deviations of PET/HTPB blend sample extruded with 300 rpm twin-screw rotating speed is always lower than samples extruded with 200 rpm and 400 rpm twin-screw rotating speeds. 300 rpm is the suggested twin-screw rotating speed for extrusion of PET by this Werner & Pfleiderer ZSK-30 twin-screw co-rotating extruder. This observation indicates that the distributions of HTPB molecule in the PET/HTPB blends extruded with 300 rpm twin-screw rotating speed is more stable than those of extruded with 200 rpm and 400 rpm twin-screw rotating speeds. In the Figure 4-7 and Figure 4-8, the relative peak areas of olefin group in the sample extruded with 300 rpm twin-screw rotating speed have less increase than the increase of olefin groups in the samples extruded with 200 rpm and 400 rpm twin-screw rotating speeds. As a result, a possible reason for the initial increase trend of olefin groups in the oxidation test of PET/HTPB blends can be attributed to the uneven distributions of HTPB in the PET/HTPB blends.
Figure 4-9: Box Plots of Trans- Olefin group lose rates at different twin-screw rotating speed
(a) Temperature: 70°C rotating speed: 200 rpm (b) Temperature: 70°C rotating speed: 300 rpm (c) Temperature: 70°C rotating speed: 400 rpm (d) Temperature: 55°C rotating speed: 200 rpm (e) Temperature: 55°C rotating speed: 300 rpm (f) Temperature: 55°C rotating speed: 400 rpm
Figure 4-10: Comparison of standard deviations in the 70°C and 55°C oxidations of PET/HTPB blends with different twin-screw rotating speeds
(a) Standard deviations in the 70°C oxidation
(b) Standard deviations in the 55°C oxidation
4.3.4 Catalyst effects in the oxidation

Catalyst, especially transition metal catalyst, can affect oxidation kinetics. In this project, cobalt(II) stearate was used to examine catalyst effects on the oxidation kinetics of PET/HTPB blends. The molecular structure of cobalt(II) stearate is

\[
\left( \text{CH}_3 \text{ (CH}_2\text{)}_{15} \text{ CH}_2 - \text{C} = \text{O} \right)_2 \text{Co}
\]

PET (HP 806, 0.84 I.V.) was extruded with 5 wt% HTPB (2,800 g/mol) and 100 ppm, 200 ppm, 300 ppm cobalt stearate. One sample of PET/5 wt% HTPB blend without catalyst was collected as a control sample. Five pellets of each blend were randomly chosen and pressed into films.

Then films of PET/HTPB blends were put into a forced-air-circulation oven to conduct oxidation tests at 40ºC, 55ºC and 70ºC. Each four hours a sample film was taken out of the forced air-circulation oven to perform an ATR spectrum scan. Spectra were acquired with an FTIR spectrometer (BOMEM MB155) using 4 cm\(^{-1}\) resolution, 20 scans per minute in the 500 cm\(^{-1}\) to 4000 cm\(^{-1}\) range. ATR spectra are obtained to monitor change of olefin group of HTPB (973 cm\(^{-1}\)) and carbonyl group (1713 cm\(^{-1}\)).

Figure 4-11, Figure 4-12 and Figure 4-13 show the change of olefin group of blends during 70ºC, 55ºC and 40ºC oxidation tests. Decreasing curves of trans-olefin groups (973 cm\(^{-1}\)) are considered as first order reactions and natural logarithm conversion was applied. Rate constants of decreasing of trans-olefin group (973 cm\(^{-1}\)) were calculated
as shown in Table 4.5.

Figure 4-11: Trans C=C olefin group in 70°C oxidation test
Figure 4-12: Trans C=C olefin group in 55°C oxidation test

Figure 4-13: Trans C=C olefin group in 40°C oxidation test
Table 4-5: Oxidation rate constants for PET/HTPB blends with catalyst at 70°C and 55°C

<table>
<thead>
<tr>
<th>Catalyst Concentration (ppm)</th>
<th>Oxidation temperature (°C)</th>
<th>Trans-olefin decreasing rate (per hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>70</td>
<td>-0.00214</td>
</tr>
<tr>
<td>100</td>
<td>70</td>
<td>-0.00241</td>
</tr>
<tr>
<td>200</td>
<td>70</td>
<td>-0.00206</td>
</tr>
<tr>
<td>300</td>
<td>70</td>
<td>-0.00245</td>
</tr>
<tr>
<td>Control</td>
<td>55</td>
<td>-0.001100</td>
</tr>
<tr>
<td>100</td>
<td>55</td>
<td>-0.001025</td>
</tr>
<tr>
<td>200</td>
<td>55</td>
<td>-0.001035</td>
</tr>
<tr>
<td>300</td>
<td>55</td>
<td>-0.001165</td>
</tr>
<tr>
<td>Control</td>
<td>40</td>
<td>-0.000363</td>
</tr>
<tr>
<td>100</td>
<td>40</td>
<td>-0.000341</td>
</tr>
<tr>
<td>200</td>
<td>40</td>
<td>-0.000346</td>
</tr>
<tr>
<td>300</td>
<td>40</td>
<td>-0.000301</td>
</tr>
</tbody>
</table>

From Trans-olefin group decreasing rate of Table 4-5, there is no obvious difference of trans-olefin group decreasing rate between control sample and blends sample with catalyst. Cobalt catalyst did not affect rate of losing olefin double bonds at these two oxidation temperatures.

In the 70°C oxidation test, some samples have obvious oxidation induction times before which there is no sign of oxidation. The control sample without catalyst has a 16 hours oxidation induction time; the sample with 100 ppm catalyst has an 8 hours oxidation time; the sample with 200 ppm catalyst has a 24 hours oxidation time and the sample with 300 ppm catalyst has no oxidation induction time. In the 70°C oxidation test, there is no clear difference between control sample which does not contain catalyst and other samples with catalyst.

In the 55°C oxidation test, the control sample has a 20 hours oxidation induction time; the
sample with 100 ppm catalyst has no oxidation time; the sample with 200 ppm catalyst has a 60 hours oxidation time and the sample with 300 ppm catalyst has a 40 hours induction time. In the 55°C oxidation test, the sequence of oxidation induction time is: sample with 100 ppm catalyst, control sample without catalyst, sample with 300ppm catalyst and sample with 200ppm catalyst. There is still no clear clue of catalyst effect on the oxidation induction time of PET/HTPB blends. However, in the 40°C oxidation test the oxidation induction times of control sample and sample with catalyst are obviously different.

Oxidation Induction Time:

- The control sample (without catalyst): 400 hours
- Sample with 100ppm catalyst: 160 hours
- Sample with 200ppm catalyst: 0 hours
- Sample with 300ppm catalyst: 0 hours

In the 40°C oxidation test of PET/HTPB blend samples, samples with catalyst have obviously shorter oxidation induction times than that of a control sample without catalyst. In the 40°C oxidation test, the oxidation reaction is slow which help distinguishing oxidation induction times.
4.4 Oxidation by-products

In the previous research of oxidation kinetics of PET/HTPB blends, the concentration of carbonyl group which is the final oxidation product was found fluctuating during oxidation or decreasing after oxidation is finished. Small molecules of oxidation products which can be released into atmosphere was suspected. In this portion of the research, gas chromatography-mass spectrometry (GC-MS) was used to identify the oxidation by-product which can be released from PET/HTPB blend into the atmosphere during the oxidation. Three GC glass sample bottles were prepared: first one contained PET/5wt%HTPB blends powder; the second one contains 0.1 gram pure liquid polybutadiene (1200 g/mol); the last GC sample bottle contains air as reference. The three GC sample bottles were put into an oven to oxidize at 50°C for 10 days. After 10 days of oxidation, a GC syringe was used to take out 2 microliters of gas from each GC sample and injected into Hewlett Packard (5890) GC-MS machine to run GC-MS spectrum. The spectrum of the third GC sample bottle which only contains pure air is used as reference.

Figure 4-14 and Figure 4-15 show the GC-MS spectrum of the gas phase oxidation by-products of PET/HTPB blends and pure liquid polybutadiene respectively. These two spectra show two major gas compounds with molecular weights of 28 and 44. The gas with molecular weight of 28 is nitrogen. The gas with molecular weight of 44 could be carbon dioxide or acetaldehyde.
The average carbon dioxide concentration in atmosphere is 387 parts per million. However in Figure 4-14 and Figure 4-15, the intensity ratio of the unknown gas to nitrogen is 15 to 100 and 40 to 100 respectively. The concentration of this unknown gas compound should not be carbon dioxide because of its high concentration. The major gas phase oxidation by-product of PET/HTPB blend and pure liquid polybutadiene is acetaldehyde.
Figure 4-14: GC-MS spectrum of oxidation gas product of PET/HTPB blend
Figure 4-15: GC-MS spectrum of oxidation gas product of pure liquid HTPB
Chapter 5

Reactions in the Reactive Extrusion of PET and Hydroxyl Terminated Polybutadiene

5.1 Introduction

Extrusion is a common processing procedure in polymer processing. The major usage of extrusion is for melting, compounding or blending of polymers. Reactive extrusion is a polymer processing technique which uses an extruder as a chemical reactor. Chemical reactions associated with polymers can be carried out while polymers and other compounds are being blended in the extruder. Reaction temperature usually is the extrusion temperature.

The blending process of PET and hydroxyl terminated polybutadiene (HTPB) is a very important issue in this thesis. The reason for blending hydroxyl terminated polybutadiene (HTPB) and PET is that the hydroxyl end groups of HTPB are expected to react with end groups of PET to form a co-polyester during reactive extrusion. The PET/HTPB copolyester may have different optical, thermal and mechanical properties than those of a PET/PBD physical blend. The common challenge of preparing a PET/PBD blend is the formation of opaque white color of the blend. Generally, phase separation is suspected to
be the reason for the opaque optical property of a PET/PBD blend. The PET/HTPB copolyester, which is a combination of PET and polybutadiene, can enhance phase compatibility between PET and polybutadiene. The PET/HTPB copolyester can, therefore, improve the optical properties of a blend.

A series of experiments were set up to evaluate and confirm reactions between PET and hydroxyl terminated polybutadiene polymers.
5.2 Reactive Extrusion Process

The reactive extrusion process of PET and HTPB, PET resins were carried out in the twin screw extruder. A Werner & Pfleiderer (ZSK-30) co-rotating twin-screw extruder was used for reactive extrusion. The temperatures of the five zones of the twin screw extruder were 280°C. The main screw speed was 300 rpm. A liquid pump (Model CH-83) was used to inject liquid HTPB into the twin-screw extruder. The liquid pump’s flow rate curve was carefully calibrated with HTPB liquid. Extruded HTPB/PET blend from the twin strand die was immediately quenched to roughly 15°C in quench water and pelletized through pelletizer. Figure 5-1 shows the experimental setup of reactive extrusion process of PET and HTPB. The detailed description of the apparatus is given in Appendix B.

The co-rotating twin screw extruder is the ideal vessel as a reactor for PET and HTPB in which extrusion and reactions can be carried out simultaneously. The two co-rotating screws in this twin extruder has the advantage of high pumping and mixing efficiency, high torque of screw rotating and intermeshing of screw. Through the twin-screw extrusion, HTPB was supposed to be distributed evenly in the PET and reacted with PET at 280°C.
Figure 5-1: Experimental setup of twin-screw reactive extrusion
5.3 NMR method to study the reactions between PET and HTPB

NMR (Nuclear magnetic resonance) is an analysis method of studying phenomenon which occurs when the nuclei of certain atoms are immersed in a static magnetic field and exposed to a second oscillating magnetic field. The NMR phenomenon can be used to study the composition of a material.

To study the reactions between PET and HTPB, a series of PET/HTPB blend samples were prepared through reactive extrusion process. The HTPB was a liquid with a number average molecular weight of 1200 gram per mole. The PET resin (Voridian Aqua PET WA314) was a commercial PET resin supplied by Eastman Chemical with intrinsic viscosity of 0.72 dL/g. The weight concentrations of HTPB in the PET/HTPB blends were 1 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt%.

First, 400 MHZ proton NMR spectra of pure hydroxyl terminated polybutadiene and PET were obtained as shown in Figure 5-2 and Figure 5-3. A 400 MHZ proton NMR spectrum of PET with 1% wt HTPB blend was obtained as shown in Figure 5-4.
Figure 5-2: 400 MHZ proton NMR spectrum of hydroxyl terminated polybutadiene (HTPB, \( M_n = 1200 \) g/mol) (solvent: d-Chloroform)
In Figure 5-2, the doublet appearing at \((\delta=5.43\text{ppm}, 5.40\text{ppm})\) represents proton of cis- or trans- olefin group of HTPB; the doublet appearing at \((\delta=2.09\text{ppm}, 2.04\text{ppm})\) represents proton of CH$_2$ methyl group of HTPB; Some small singlets \((\delta=1.30\text{ppm}, 1.45\text{ppm}, 4.32\text{ppm}, 4.80\text{ppm}, 5.57\text{ppm})\) represent 1,2 butadiene group (vinyl olefin) in HTPB.
Figure 5-3: 400 MHz 1H NMR Spectra of pure PET (solvent: 30 wt% d-TFA, 70 wt% d-Chloroform)
The NMR spectrum of pure PET is Figure 5-3. The singlet appearing at (δ=4.79ppm) represents proton of methyl group in the PET chain. The singlet appearing at (δ=8.12ppm) represents proton of an aromatic ring in the PET chain.

In the Figure 5-4, the spectrum of PET with 1wt% HTPB blend seems to have no difference with Figure 5-3 which is the spectrum of pure PET. However, in Figure 5-5 (a) and Figure 5-5 (b), when both NMR spectra of pure PET and PET with 1wt% HTPB blend were magnified 30 times, chemical shifts of polybutadiene in the blend can be observed in Figure 5-5 (b). In Figure 5-5 (b), singlet (δ=5.44ppm) represents the proton of an olefin group of polybutadiene and a tiny singlet (δ=2.05ppm) represents proton of the CH₂ methyl group of polybutadiene in the PET/HTPB blend.
Figure 5-4: 400 MHz 1H NMR Spectra of PET with 1wt% HTPB Blend (solvent: 30 wt% d-TFA, 70 wt% d-Chloroform)
Figure 5-5: 400 MHz 1H NMR Spectra of PET (a) and PET with 1wt% HTPB Blend (b) (solvent: 30 wt% d-TFA, 70 wt% d-Chloroform)
The reactions between PET and HTPB were expected to occur between end groups of PET and HTPB. In other words, reactions may only occur at the ends of each molecule. The repeat units of PET molecule and polybutadiene molecule are shown in Figure 5-6 and proton locations on the repeat unit are also labeled.

![Figure 5-6: Proton locations on the repeat units PET and Polybutadiene molecules](image)

If a reaction between PET and HTPB did occur, both the chemical shift of proton (1) of the PET molecule and the chemical shift of proton (1) of the HTPB molecule should change. Both PET and HTPB are polymers. For the PET used in this experiment (typical I.V. is 0.72 dl/g, Mn=24305 g/mol), one PET molecule should have approximately 129 repeat units. In other word, for PET, only 1 of 129 protons’ chemical environment may be changed due to reaction between PET and HTPB. For HTPB (Mn=1200 g/mol), one molecule should have approximately 21 repeat units. If reaction did occur, 1 of 21 protons’ chemical environment may be changed due to reaction between PET and HTPB. After comparison of structure, HTPB has shorter molecule than PET and HTPB would have more obvious chemical shift change of proton in NMR spectrum.
Software (ACD/Chemsketch 10.0) was used to predict the position of the ester link between PET and HTPB. This software simulation predicted that a new chemical shift of protons on HTPB molecule should be found at 4.95 ppm due to the influence of ester link between PET and HTPB in 600 MHZ proton NMR spectrum as Figure 5-7 shows.

Figure 5-7: ACD/Chemsketch 10.0 software’s prediction of new chemical shift of protons on HTPB molecule due to the influence of ester link between PET and HTPB
The 600 MHZ proton NMR spectra of pure PET and high M.W. PET/HTPB blends with 1.0, 2.0, 3.0, 4.0 and 5.0 wt% HTPB were obtained in Figure 5-8. In the spectra of the blends, a new chemical shift at 4.95 ppm was found as software (ACD/Chemsketch 10.0) predicted. All proton NMR spectra of HTPB in chloroform solvent and d-TFA solvent do not have this chemical shift. Similarly the proton NMR spectrum of pure PET does not have this chemical shift. It is clear that this chemical shift at 4.95ppm was the evidence of an ester link between PET and HTPB.

If esterification reaction happened between PET and HTPB, the ester linkage would influence both the chemical shifts of protons on HTPB’s molecule and protons on PET’s aromatic ring. Due to the influence of ester linkage between PET and polybutadiene molecules as Figure 5-9 shows, the proton on polybutadiene methylene which is adjacent to the ester linage should have new chemical shift at 4.95 ppm and the proton on the
aromatic ring of PET molecule should have a new chemical shift at 8.70 ppm. In Figure 5-8, HTPB’s methylene proton had a tiny but noticeable chemical shift at 4.95 ppm after extrusion with PET. However, no change of PET’s aromatic proton was found in Figure 5-8. The possible reason is that the concentration of ester linkage in the PET/HTPB blend which have reacted to form a copolymer was low which only influence very few amounts of protons on the aromatic rings of the PET molecule. Two dimensional NMR Spectrum, correlation spectroscopy (COSY), was used to verify if there was a reaction that connect PET molecule and HTPB molecule. COSY is one type of two-dimensional nuclear magnetic resonance (NMR) spectroscopy which can determine if two peaks are bonded due to chemical relationship. However, due the same reason of very low concentration of polybutadiene in the PET/HTPB blends, no peaks of polybutadiene was observed in the COSY spectrum to verify reactions between PET and polybutadiene.
Figure 5-9: Chemical Structure of ester linkage between PET and HTPB
To observe the influence of the ester linkage on the PET molecule, the concentration of HTPB in the PET/HTPB blend was increased to a high value. HP806 PET resin (0.84 I.V.) was manually mixed with 20 wt% liquid HTPB (1200 g/mol). Then the PET resin and liquid HTPB mixture was extruded with a Werner & Pfleiderer (ZSF-30) co-rotating twin-screw extruder. In the twin-screw extrusion of PET/20wt% HTPB mixture, the concentration of liquid HTPB is beyond the processing limit of the twin-screw extruder. Some amount of liquid HTPB vaporized during twin-screw extrusion and the vacuum pump on the twin-screw extruder had to be turned on to evacuate HTPB vapor.

After twin-screw extrusion, the extruded PET/HTPB blends pellets were ground into powder, dissolved in 30% d-TFA/70% d-Chloroform solvent and scanned with a 600 MHZ proton NMR. The 600MHZ proton NMR spectrum of this blend shows that the integral area of doublet 2.09 ppm (methylene proton of HTPB) is 13.9 times of that area in the PET/1 wt% HTPB sample. The integral area of doublet 5.43 ppm (proton of HTPB’s olefin group) is 12.9 times of that area in the PET/1 wt% HTPB sample. The final concentration of HTPB in this PET/HTPB blend was approximately 13.5 wt%. Nearly 6.5 wt% of liquid HTPB was vaporized and evacuated by the vacuum pump in the twin-screw extruder.

Two new and sharp chemical shifts of aromatic protons of PET molecule which is adjacent to ester linkage was found in the 600MHZ proton NMR spectrum of this PET with 13.5 wt% HTPB blend. The two new chemical shifts are 8.73ppm and 8.69 ppm as Figure 5-10 shows.
Base on the new chemical shifts of aromatic protons on PET found in Figure 5-10, previous proton NMR spectra of 1-5wt% HTPB and PET blends was magnified 20 times from 8.3 ppm to 9 ppm range in Figure 5-11, the new chemical shift of aromatic proton on PET molecule due the influence of ester linkage can be identified around 8.7 ppm although it is almost overwhelmed by spectrum noise.
HTPB’s methylene proton had been identified as a new tiny chemical shift at 4.95 ppm in the 600MHZ proton NMR spectrum of 1 to 5 wt% PET/HTPB blends. Two new chemical shifts of aromatic protons on the PET molecule at 8.73 ppm and 8.69 ppm which are adjacent to ester linkage were found in the 600MHZ proton NMR spectrum of PET with 13.5 wt% HTPB blend. All the new chemical shifts fit the suspicion that the ester linkage will influence both the chemical shifts of HTPB’s methylene proton and PET’s aromatic proton when esterification reaction did happen between PET and HTPB. 600MHZ proton NMR spectra successfully confirmed all new chemical shifts due to reactions between PET and HTPB.
5.4 FTIR method to study reactions between PET and HTPB

Infrared spectroscopy (IR spectroscopy) studies the infrared region of electromagnetic absorption spectrum. When an infrared light interacts with sample material, chemical groups of this material will absorb infrared radiation in a specific wave number. With this radiation energy, chemical groups of sample material will stretch, contract or bend at specific frequencies. The resonant frequencies and intensities can be used to identify chemical groups in the test sample. PET molecule has two end groups which are carboxyl end group and hydroxyl end group. One hydroxyl terminated polybutadiene (HTPB) molecule has two hydroxyl groups. FTIR method was used to verify reactions between PET and hydroxyl terminated polybutadiene. Since reactions between PET and HTPB were suspected to happen between the end groups of the two materials, the end group analysis method is used to study reactions between PET and HTPB.

To study the reactions between PET and HTPB, two PET resins with different intrinsic viscosities were used to blend with HTPB through the twin screw extruder. The PET resins have intrinsic viscosity of 0.72 dL/g and 0.48 dL/g respectively. The high I.V. PET resin (Voridian Aqua PET WA314, I.V.=072 dL/g) is supplied by Eastman Chemical. The lower I.V. PET resin (I.V.=0.48 dL/g) is a twin-screw extrusion degradation product of WA314 PET resin. HTPB is a liquid hydroxyl terminated polybutadiene with molecular weight of 1,200 g/mol purchased from Sigma-Aldrich. Blends of high M.W. PET (0.72
dL/g) and HTPB with HTPB concentrations of 1 wt% to 5.0 wt% with 1 wt% as increasing step were prepared. Similarly, blends of low M.W. PET (0.48 dL/g) and HTPB with HTPB concentrations of 1 wt% to 5 wt% with 1 wt% as increasing step were prepared through twin-screw extrusion.

5.4.1 FTIR end group analysis of PET

Before studying end groups of PET/HTPB blends, end group analysis of PET was preformed based on FTIR end group analysis of PET which is developed by Sami Al-abdulRazzak [99]. Carboxyl and hydroxyl end groups are two major end groups of PET. This FTIR method to determine carboxyl and hydroxyl end group values has been proven successful. This technique uses a subtraction method between FTIR spectra of a dry PET film and its deuterated film to determine values of two end group of PET. When PET film is soaked in heavy water (deuterium oxide) at 50°C more than 24 hours, hydrogen atom of PET’s two end groups will be replaced by deuterium atom of heavy water. The replacement of end group hydrogen atom by deuterium atom will generate zero absorbance in the end groups section of FTIR spectrum. Then a subtraction spectrum between dry PET film and its deuterated film can reveal values of two end group of PET in FTIR spectrum.

PET pellets were pressed into film. Film size is around 5×5 mm and thickness is under 0.3 mm. All films were dried in the vacuum oven under 50°C for 20 hours. Because PET and its blend is strongly hydrophilic, only one dry film was taken out from vacuum oven
each time and scanned by Fourier transform infrared spectrophotometer (Perkin Elmer 1600 series) in the range of 550 cm\(^{-1}\) to 4000 cm\(^{-1}\) with 20 scans per sample. The FTIR spectrophotometer is equipped with a nitrogen gas purge in the sample holder chamber which can reduce moisture absorbance during scanning. After scanning spectra of dry PET and PET/HTPB blends films, thickness of all films were measured and recorded. Then all the film samples were put into flask which contains deuterium oxide (heavy water) to begin deuteration at 50°C. The deuteration process takes approximately 24 hours. The diagram of experimental set-up of deuteration is shown in Figure 5-12. The high purity nitrogen pure can prevent heavy water from absorbing atmospheric moisture during deuteration. After deuteration was finished, only one film sample was taken out of flask each time and scanned by FTIR.
Figure 5-12: Experiment setup of deuteration

Figure 5-13 shows two spectra of dry PET film and deuterated PET film. They only had two obvious differences in the regions of 2700-2400 cm\(^{-1}\) and 3700-3100 cm\(^{-1}\). In the dry PET FTIR spectrum, the region from 3700-3100 cm\(^{-1}\) is the absorbance of hydrogen atom of carboxyl and hydroxyl end groups (-COOH and -OH). When PET sample film is deuterated, the absorbance of newly formed deuterium atoms of –COOD and –OD end groups shift to region 2700-2400 cm\(^{-1}\). As a result, the absorbance of PET two end groups in the region 3700-3100 cm\(^{-1}\) become zero. Therefore, subtracting dry PET spectrum by deuterated PET spectrum in the region 3100-3700 cm\(^{-1}\) can get hydroxyl and carboxyl end groups absorbance. Figure 5-14 shows the spectra subtraction result of dry PET film.
and its deuterated film in the region from 3700-3100 cm$^{-1}$.

Figure 5-13: FTIR spectra of dry PET and deuterated PET film

Figure 5-14 is the FTIR spectra subtraction result of dry PET film and its deuterated film in the region from 3700-3100 cm$^{-1}$.

Figure 5-14 shows two peaks. One is hydroxyl (-OH) end group of PET, the peak wave number is at 3540 cm$^{-1}$. The other is carboxyl (-COOH) end group of PET, the peak wave number is at 3271 cm$^{-1}$.
Figure 5-14: Spectrum subtraction of dry PET film and its deuterated film
Based on the Beer-Lambert law, \( A = a(\lambda) \times b \times c \), where \( A \) is the measured absorbance in FTIR spectrum, \( a(\lambda) \) is a wavelength-dependent absorptivity coefficient, \( b \) is the path length, and \( c \) is the concentration. The unit of vertical coordinate in the origin FTIR spectrum of PET end groups (Figure 5-14) is absorbance. Each sample measured in FTIR had its thickness and value of vertical coordinate depended on the thickness of FTIR measured sample. To eliminate the thickness influence in the FTIR spectrum, the vertical coordinate had been normalized to the thickness of sample. For example, unit of vertical coordinate of Figure 5-14 is Absorbance. In Figure 5-15, unit of vertical coordinate is divided by the thickness of measure PET film sample which is 0.018 centimeter. The unit of vertical coordinate became Absorbance/cm which is a normalization result. This method eliminated the sample thickness influence in the FTIR spectrum. All the following FTIR spectra and their calculations in this thesis had been normalized to the sample thickness.
From Figure 5-14 and Figure 5-15, two end groups of PET have been identified in the subtraction FTIR spectrum. The peak at 3540 cm$^{-1}$ is the hydroxyl end group of PET and the peak at 3271 cm$^{-1}$ is the carboxyl end group of PET. These two peaks overlap each other in a small range around 3400 cm$^{-1}$. Gaussian simulation can resolve the problem of overlapping peaks. Figure 5-16 shows a Gaussian simulation of the two peaks: carboxyl end group and hydroxyl end groups of PET.
Figure 5-16: Gaussian simulation of carboxyl and hydroxyl end group of PET

In Sami Al-abdulRazzak\cite{99}’s paper, a correlation between FTIR Gaussian simulation and independent titration method was successfully developed. The accuracy of FTIR Gaussian simulation is acceptable. For example, in Sami Al-abdulRazzak\cite{99}’s paper, to determine carboxyl end group value, the difference between FTIR Gaussian simulation and independent titration method is from 3.1% to 12.0%. To determine hydroxyl end group value, the difference between FTIR Gaussian simulation and independent titration method is from 4.8% to 15.3%. Because titration method is time consuming, using FTIR method with Gaussian simulation is a reliable choice.
5.4.2 FTIR end group analysis of HTPB

FTIR spectrum of pure liquid HTPB can be obtained by using a device as shown in Figure 5-17. Two potassium bromide plates were used to sandwich a spacer ring. The thickness of the spacer ring is 0.11 mm. A background FTIR spectrum is obtained when the spacer ring was empty. Then pure liquid HTPB was dropped into spacer ring to get a FTIR spectrum.

![FTIR device of measuring FTIR spectrum of pure liquid HTPB](image)

Figure 5-17: FTIR device of measuring FTIR spectrum of pure liquid HTPB

Figure 5-18 shows the FTIR spectrum of hydroxyl end group of pure liquid HTPB. The spectrum in Figure 5-18 has been normalized by the thickness of the spacer ring. The unit of the vertical coordinate is absorbance/cm.
Figure 5-18: FTIR spectrum of pure liquid HTPB in the region of 3712 cm\(^{-1}\) to 3100 cm\(^{-1}\)

### 5.4.3 FTIR end group analysis of PET/HTPB blends

FTIR spectra of PET and HTPB indicated that the hydroxyl end group of PET located within the range from 3712 cm\(^{-1}\) to 3413 cm\(^{-1}\) and carboxyl end group of PET is located from 3413 cm\(^{-1}\) to 3100 cm\(^{-1}\). The hydroxyl end group of HTPB was found located in the range from 3712 cm\(^{-1}\) to 3100 cm\(^{-1}\). Since all the end groups of PET and HTPB are located in the range from 3712 cm\(^{-1}\) to 3100 cm\(^{-1}\) in the FTIR spectra, the infrared response peak of this region represent the three end groups, carboxyl group of PET, hydroxyl end group of PET and hydroxyl end group of HTPB, overlapping each other. Figure 5-19 shows the three end groups of a PET/5wt\% HTPB blend sample in the range from 3712 cm\(^{-1}\) to 3100 cm\(^{-1}\) of the FTIR spectrum.
Gaussian simulation method can simulate each end group based on its peak position and peak width. Mathematically, absorption peak in IR spectrum can be performed by curve fitting of Gaussian equation. Gaussian peak fitting technique has several equations. In this project, a four parameters Gauss peak fitting equation (Gauss-amp) was used as equation (5.1) shown.

$$y = y_0 + A \times e^{-\frac{1}{2} \times \left(\frac{x-x_c}{w}\right)^2}$$  

Equation (5.1)

Where:

- $y_0$ is start value of horizontal baseline.
A is height of peak (Absorbance/cm)

\( x_c \) is position of peak’s summit (1/cm)

\( w \) is half width of peak (1/cm)

Baseline correction at point 3712 cm\(^{-1}\) has been performed on all spectra, therefore, \( y_0 \) is zero for all cases. Data analysis software – Origin Pro 7.5 ® - is used to curve fit the FTIR absorbance peaks of all end groups.

For hydroxyl end group of HTPB, single peak fitting by equation (5.1) can be used. Figure 5-20 shows peak fitting of the hydroxyl end group of HTPB. For pure HTPB (1,200 g/mol), parameters are: \( A=142.0, x_c=3356 \) and \( W=114.43 \).

Figure 5-20: End group Gaussian simulation of hydroxyl end group of HTPB
For hydroxyl and carboxyl end groups of PET, because hydroxyl and carboxyl end groups of PET have a small region where two peaks influence each other, a two peaks Gauss peak fitting equation was used.

\[ y = A_1 \times e^{-\frac{1}{2}\left(\frac{x-x_{c1}}{w_1}\right)^2} + A_2 \times e^{-\frac{1}{2}\left(\frac{x-x_{c2}}{w_2}\right)^2} \]  

Equation (5.2)

Where:

- \( A_1 \) is peak height of hydroxyl end group of PET
- \( A_2 \) is peak height of carboxyl end group of PET
- \( x_{c1} \) is position of peak’s summit of hydroxyl end group of PET
- \( x_{c2} \) is position of peak’s summit of carboxyl end group of PET
- \( w_1 \) is half width of peak of hydroxyl end group of PET
- \( w_2 \) is half width of peak of carboxyl end group of PET

Figure 5-21 shows peak fitting of the hydroxyl end groups and the carboxyl end groups of PET. For high M.W. PET (I.V. = 0.72 dL/g), parameters are: \( A_1 = 12.3 \), \( x_{c1} = 3544 \), \( w_1 = 29 \), \( A_2 = 4.0 \), \( x_c = 3288 \), \( w_2 = 75 \). For low M.W. PET (I.V. = 0.48 dL/g), parameters are \( A_1 = 15.3 \), \( x_{c1} = 3544 \), \( w_1 = 32 \), \( A_2 = 6.7 \), \( x_c = 3288 \), \( w_2 = 75 \).
Figure 5-21: End group Gaussian simulations of hydroxyl end group of PET and carboxyl end group of PET

For a PET/HTPB blend, there are three end groups in the blend which are hydroxyl end group of PET, carboxyl end group of PET and hydroxyl end group of HTPB. Peak of hydroxyl end group of PET is from 3712 cm$^{-1}$ to 3413 cm$^{-1}$; carboxyl end group of PET is from 3413 cm$^{-1}$ to 3100 cm$^{-1}$ and hydroxyl end group of HTPB is from 3712 cm$^{-1}$ to 3100 cm$^{-1}$. These three peaks influence with each other in FTIR spectrum of PET/HTPB blend. Fortunately each of these three peaks has a different position of peak summit ($x_c$)
and different half peak width (w). Gaussian peak fitting method still can be used to fit three end groups of PET/HTPB blends. A three peaks fitting equation, equation (3), is developed.

\[
y = A_1 \times e^{-\frac{1}{2} \left( \frac{x - x_{c1}}{w_1} \right)^2} + A_2 \times e^{-\frac{1}{2} \left( \frac{x - x_{c2}}{w_2} \right)^2} + A_3 \times e^{-\frac{1}{2} \left( \frac{x - x_{c3}}{w_3} \right)^2}
\]

Equation (5.3)

Where:

- $A_1$ is peak height of hydroxyl end group of PET
- $A_2$ is peak height of carboxyl end group of PET
- $A_3$ is peak height of hydroxyl end group of HTPB
- $x_{c1}$ is position of peak’s summit of hydroxyl end group of PET
- $x_{c2}$ is position of peak’s summit of carboxyl end group of PET
- $x_{c3}$ is position of peak’s summit of hydroxyl end group of HTPB
- $w_1$ is half width of peak of hydroxyl end group of PET
- $w_2$ is half width of peak of carboxyl end group of PET
- $w_3$ is half width of peak of hydroxyl end group of HTPB

To simplify equation (5.3), all parameter of w and $x_c$ were substituted by using parameters obtained from pure materials. This simplification is based on assumptions that any absorption peak will have same peak summit position and width in pure material and in blends. After simplification, equation (5.4) is derived from equation (5.3).
\[ y = A_1 \times e^{-\frac{1}{2}(x-3544)^2} + A_2 \times e^{-\frac{1}{2}(x-3288)^2} + A_3 \times e^{-\frac{1}{2}(x-3356)^2} \]  

Equation (5.4)

Where:

- \( A_1 \) is peak height of hydroxyl end group of PET
- \( A_2 \) is peak height of carboxyl end group of PET
- \( A_3 \) is peak height of hydroxyl end group of HTPB

Equation (5.4) was used for curve fitting FTIR spectra of end groups in PET/HTPB blends.

Similarly, data analysis software – Origin Pro 7.5 ® - was used to fit curves of FTIR absorbance peaks of end groups. Equation (5.4) was input into software and peak fitting function was performed. \( A_1, A_2 \) and \( A_3 \) are obtained for each PET/HTPB blends through least square fitting of Gaussian simulation. Figure 5-22 shows a curve fitting example of low M.W. PET/HTPB blend with 4.0 wt% HTPB.
Figure 5-22: End group Gaussian simulations of hydroxyl end group of PET, carboxyl end group of PET and hydroxyl end group of HTPB in the PET/HTPB blends

Table 5-1 list all curve fitting results of high M.W. PET/HTPB blends and Table 5-2 list all curve fitting results of low M.W. PET/HTPB blends.
### Table 5-1: Peak fitting results of high M.W. PET (0.72 dL/g) /HTPB blends

<table>
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<th>Material</th>
<th>End group</th>
<th>Xc (cm(^{-1}))</th>
<th>W (cm(^{-1}))</th>
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<td>3544</td>
</tr>
<tr>
<td></td>
<td>COOH of PET</td>
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<td></td>
<td>OH of HTPB</td>
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<td></td>
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<tr>
<td></td>
<td>OH of HTPB</td>
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</tr>
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Table 5-2: Peak fitting results of low M.W. PET (0.48 dL/g) /HTPB blends

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<th>W (cm(^{-1}))</th>
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<td>114.43</td>
</tr>
<tr>
<td>Low M.W. PET/HTPB Blends with 3.0 wt% HTPB</td>
<td>OH of PET</td>
<td>21.14</td>
<td>3544</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>COOH of PET</td>
<td>5.83</td>
<td>3288</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>OH of HTPB</td>
<td>2.60</td>
<td>3356</td>
<td>114.43</td>
</tr>
<tr>
<td>Low M.W. PET/HTPB Blends with 4.0 wt% HTPB</td>
<td>OH of PET</td>
<td>22.80</td>
<td>3544</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>COOH of PET</td>
<td>4.85</td>
<td>3288</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>OH of HTPB</td>
<td>4.46</td>
<td>3356</td>
<td>114.43</td>
</tr>
<tr>
<td>Low M.W. PET/HTPB Blends with 5.0 wt% HTPB</td>
<td>OH of PET</td>
<td>23.24</td>
<td>3544</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>COOH of PET</td>
<td>3.44</td>
<td>3288</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>OH of HTPB</td>
<td>8.20</td>
<td>3356</td>
<td>114.43</td>
</tr>
</tbody>
</table>
Curve fittings of FTIR spectra for end groups in the PET/HTPB blend were finished by Gauss three peaks simulation through Equation (5.4). In Sami Al-abdulRazzak’s paper, he developed the correlation of normalized peak area of hydroxyl end group of PET and carboxyl end group of PET with actual titration result. Normalized peak area means peak area is the peak area which was divided by sample thickness. In Sami Al-abdulRazzak’s paper, correlation of normalized peak area of hydroxyl end group of BHET and titration result was:

\[ C_{\text{OH}} \times 10^{-6} \text{ mol/g} = \frac{\text{Normalized Area of OH end group (absorbance/cm}^2\text{)}}{0.096} \]

Equation (5.5)

Correlation of normalized peak area of hydroxyl end group of PET and titration result was:

\[ C_{\text{COOH}} \times 10^{-6} \text{ mol/g} = \frac{\text{Normalized Area of COOH end group (absorbance/cm}^2\text{)}}{0.028} \]

Equation (5.6)

In FTIR spectrum of PET/HTPB blends, normalized peak area of hydroxyl end group of PET and carboxyl end group of PET can be easily obtained through integration of their peak functions. For each individual peak, peak area can be calculated by equation (5.7):

\[ \text{Area} = \int_{-\infty}^{\infty} y \, dx = \int_{-\infty}^{\infty} A \times \exp\left(-\frac{1}{2} \times \left(\frac{x-x_c}{w}\right)^2\right) \, dx = A \times w \times \sqrt{2\pi} \]

Equation (5.7)

Since parameters of three end groups in each PET/HTPB blend has been calculated in Table 5-1 and Table 5-2, peak areas of each individual end groups can be easily
calculated through Equation (5.7). After peak areas of individual end groups in the blend were obtained, the actual concentration of each end group can be calculated through the correlation Equation (5.5) and (5.6).

The FTIR spectra of pure PET and pure HTPB were already obtained. For high molecular weight PET (0.72 I.V.), the concentration of hydroxyl end groups is 85.8 (10^{-6} mol/g) and the concentration of carboxyl end groups is 21.1 (10^{-6} mol/g). For the pure HTPB, the concentration of hydroxyl end groups was 1667 (10^{-6} mol/g). For a PET/HTPB blend, if there was no reaction between end groups of PET and HTPB, each end group’s concentration can be easily calculated based on each material’s contribution in the blend. For example, for a high M.W. PET/HTPB blend with 5 wt% HTPB concentration, if no reaction happened between end groups of PET and HTPB:

The hydroxyl end group of PET = 85.8 (10^{-6} mol/g) × (1-0.05) = 81.5 (10^{-6} mol/g)

The carboxyl end group of PET = 21.1 (10^{-6} mol/g) × (1-0.05) = 20.0 (10^{-6} mol/g)

The hydroxyl end group of HTPB = 1667 (10^{-6} mol/g) × 0.05 = 83.4 (10^{-6} mol/g)

For each PET/HTPB blend, actual concentrations of each end groups in the PET/HTPB blends were calculated base on Gaussian simulation of experiment results. At the same time, concentrations of each end group in the PET/HTPB blends at no reaction scenario were also calculated. For each end group its actual concentration and calculated concentration at no reaction scenario were list in Table 5-3 and Table 5-4. Comparing
each end groups’ actual concentrations and calculated concentrations at no reaction scenario can reveal the reaction between end groups.

Table 5-3: Calculated end group concentrations of High M.W. PET (0.72 IV)/HTPB blends

<table>
<thead>
<tr>
<th>HTPB Concentration</th>
<th>Actual concentrations by simulation</th>
<th>Concentrations at No Reaction Scenario</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OH of PET $10^{-6}$ mol/g</td>
<td>COOH of PET $10^{-6}$ mol/g</td>
</tr>
<tr>
<td>0%</td>
<td>85.8</td>
<td>21.1</td>
</tr>
<tr>
<td>1%</td>
<td>102.8</td>
<td>10.7</td>
</tr>
<tr>
<td>2%</td>
<td>110.4</td>
<td>8.7</td>
</tr>
<tr>
<td>3%</td>
<td>121.8</td>
<td>1.3</td>
</tr>
<tr>
<td>4%</td>
<td>129.0</td>
<td>0.3</td>
</tr>
<tr>
<td>5%</td>
<td>140.0</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 5-4: Calculated end group concentrations of Low M.W. PET (0.48 IV)/HTPB blends

<table>
<thead>
<tr>
<th>HTPB Concentration</th>
<th>Actual concentrations by simulation</th>
<th>Concentrations at No Reaction Scenario</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OH of PET $10^{-6}$ mol/g</td>
<td>COOH of PET $10^{-6}$ mol/g</td>
</tr>
<tr>
<td>0%</td>
<td>117.8</td>
<td>35.3</td>
</tr>
<tr>
<td>1%</td>
<td>142.3</td>
<td>31.8</td>
</tr>
<tr>
<td>2%</td>
<td>141.5</td>
<td>34.3</td>
</tr>
<tr>
<td>3%</td>
<td>162.8</td>
<td>29.1</td>
</tr>
<tr>
<td>4%</td>
<td>175.6</td>
<td>24.1</td>
</tr>
<tr>
<td>5%</td>
<td>179.0</td>
<td>18.3</td>
</tr>
</tbody>
</table>

Figures 5-23 to 5-25 show the comparison between actual end group concentration and concentration at no reaction scenario in the high M.W. PET (0.72IV) PET/HTPB blends.
Figure 5-23: Actual concentration of carboxyl end group of PET and calculated concentration of carboxyl end group of PET at no reaction scenario in the high M.W. PET (0.72 IV)/HTPB blends.

Figure 5-24: Actual concentration of hydroxyl end group of PET and calculated concentration of hydroxyl end group of PET at no reaction scenario in high M.W. PET (0.72 IV)/HTPB blends.
Figure 5-25: Actual concentration of hydroxyl end group of HTPB and calculated concentration of hydroxyl end group of HTPB at no reaction scenario in high M.W. PET (0.72 IV)/HTPB blends

Figure 5-23 clearly showed that the carboxyl end group of PET decreased with increasing concentration of HTPB in the blends. This result indicates the esterification reaction occurred between hydroxyl end group of HTPB and carboxyl end group of PET which consumed the carboxyl end group of PET as Reaction 1 shows. Figure 5-25 also proved this result in which the actual concentration of hydroxyl end groups of HTPB was lower than no reaction scenario. This lower value of actual concentration of hydroxyl end group of HTPB also indicated esterification reaction consume hydroxyl end group of HTPB.

\[
\text{PET-COOH} + \text{HO-PBD} \rightarrow \text{PET-COO-PBD} + \text{H}_2\text{O} \quad \text{(Reaction 1)}
\]

In the Figure 5-24, the actual concentrations of hydroxyl end group of PET were higher.
than the no reaction scenario. This result shows that there exist reactions which generate hydroxyl end group of PET. The first assumption was the hydrolysis reaction which generated both carboxyl end group of PET and hydroxyl end group of PET as Reaction 2 shows. Because esterification reaction (Reaction 1) between hydroxyl end group of HTPB and carboxyl end group of PET can generate water, the water can induce the hydrolysis reaction of PET.

\[
\begin{array}{c}
\text{O} \\
\text{\underline{-C-O}} \\
\end{array} \quad \rightarrow \quad \\
\begin{array}{c}
\text{O} \\
\text{\underline{-C-OH}} + \underline{\text{OH-}} \\
\end{array}
\]

(Reaction 2)

Hydrolysis reaction was not the only explanation of increasing hydroxyl end group of PET in the blends. A transesterification reaction also can increase hydroxyl end group of PET as Reaction 3 shows. In Reaction 3, \(R'\) could be the polybutadiene segment, \(R''\) and \(R\) could be PET segment. When transesterification reaction occurred, hydroxyl end group of HTPB will be transferred to PET chain as end group. In this reaction, hydroxyl end group of HTPB will become hydroxyl end group of PET and thus increase the concentration of hydroxyl end group of PET in the blends.

\[
\begin{array}{c}
\underline{\text{R'O}} \\
\text{OH} \\
\end{array} + \\
\begin{array}{c}
\text{O} \\
\text{\underline{-C} \, \underline{\text{R}}} \\
\end{array} \quad \rightarrow \\
\begin{array}{c}
\underline{\text{R'O}} \\
\text{\underline{OH}} \\
\end{array} + \\
\begin{array}{c}
\text{O} \\
\text{\underline{-C} \, \underline{\text{R}}} \\
\end{array}
\]

(Reaction 3)

There was a reason to support the suspicion of transesterification reaction between PET and HTPB. The actual measurement of hydroxyl end group of PET in a high M.W. PET (0.72 IV)/5wt% HTPB blends is 140 \((10^{-6} \text{ mol/g})\). This hydroxyl end group of PET value
is significantly higher than any hydroxyl end group concentration of PET that has been reported. For example, a high M.W. PET (0.72 IV) resin was twin-extruded at 280°C without drying. The saturated moisture in the PET pellets generated great hydrolysis reaction in the extruder. After twin screw extrusion without necessary drying, IV of this PET decreased to 0.48 IV and the hydroxyl end group of PET only increased to 118 (10^-6 mol/g). The hydroxyl end group of PET in a high M.W. PET (0.72 IV)/5wt% HTPB blends is 140 (10^-6 mol/g) which is higher than 118 (10^-6 mol/g). This comparison shows that hydrolysis is not the only reaction that increase hydroxyl end groups of PET, a transesterification reaction was highly possible to assist generating hydroxyl end group of PET during the extrusion of blends.

In Figure 5-25, the concentrations of hydroxyl end groups of HTPB are lower than in the case of no reaction scenario. This deviation shows esterification reaction between HTPB and PET consumed hydroxyl end group of HTPB. While the hydroxyl end group concentration of HTPB approach closer to no reaction scenario when HTPB concentration increases in the blends. This phenomenon indicated that a reaction can generate hydroxyl end groups of HTPB simultaneously when the esterification reaction was consuming hydroxyl end groups of HTPB. When the concentration of HTPB in the PET/HTPB blends is high, the generating rate of hydroxyl end group of HTPB is higher than the consuming rate. A hydrolysis reaction of HTPB due to the residual oxygen and water generated by esterification reaction was suspected to generate diol hydroxyl groups
on the HTPB molecule as Reaction 4 shows.

\[ \text{\begin{align*}
- \text{C}=\text{C}^- + \text{O}_2 & \rightarrow -\text{C}\text{C}^- + \text{H}_2\text{O} \\
& \quad \rightarrow -\text{C}\text{C}^-
\end{align*}} \]

(Reaction 4)

Figures 5-26 to 5-28 show the comparison between actual end group concentrations of end groups and concentrations at no reaction scenario in the low M.W. PET (0.48IV) PET/HTPB blends. Similarly, Figure 5-26 shows that the carboxyl end groups of PET were consumed by the esterification reactions between PET and HTPB. Figure 5-27 shows that the concentration of hydroxyl end groups of PET in the blends was significantly higher than the no reaction scenario. The hydrolysis reaction of PET itself and transesterification reaction between PET and HTPB molecule generated hydroxyl end groups of PET. Figure 5-28 shows that the esterification reaction between PET and HTPB consumed some hydroxyl end groups of HTPB. While at the same time, the hydrolysis reaction of HTPB itself generates hydroxyl end groups which compensate the consumption of hydroxyl end groups of HTPB during esterification reactions between PET and HTPB molecules. The actual concentration of hydroxyl end groups of HTPB approach concentrations of the no reaction scenario. When the HTPB concentration is 5 wt% in the blends, the actual concentration of hydroxyl end group of HTPB was higher than the no reaction scenario. In this blend, hydrolysis rate of HTPB already compensates and overcomes the losing rate of hydroxyl end group of HTPB due to esterification reactions.
Figure 5-26: Actual concentration of carboxyl end group of PET and calculated concentration at no reaction scenario in low M.W. PET (0.48 IV)/HTPB blends

Figure 5-27: Actual concentration of hydroxyl end group of PET and calculated concentration at no reaction scenario in low M.W. PET (0.48 IV)/HTPB blends
In the FTIR end group analysis method used to confirm reactions between PET and HTPB, it is expected that moisture will play an important role. Both PET and HTPB may have hydrolysis reactions in the twin-screw extruder. To confirm the influence of hydrolysis reactions in the reactive twin-screw extrusion of PET/HTPB blends, a low M.W. PET (0.48 IV) and HTPB materials were twin-screw extruded without drying the PET resin.

In Figure 5-29 (a), carboxyl end groups of PET in the low M.W. PET (0.48 IV) and HTPB blends extruded with pre-drying the PET pellets begins to decrease when HTPB concentration reaches 2 wt%. In Figure 5-29 (b), carboxyl end group of PET in the low M.W. PET (0.48 IV) and HTPB blends extruded without pre-drying the PET pellets decreases in all blend samples. The decreasing of carboxyl end group of PET in the
PET/HTPB blends indicates reactions were consuming carboxyl end group of PET in the
twin-screw extrusion with and without drying. Slopes of carboxyl end group of PET
concentrations versus HTPB concentrations in the blends are the dependence of
decreasing carboxyl end group of PET on HTPB concentrations in the blends. Figure
5-29 shows that slopes of decreasing carboxyl end groups of PET versus HTPB
concentrations in the blend are similar either with drying or without drying. However,
when concentrations of carboxyl end group of PET in the two PET/HTPB blend samples
with the same HTPB concentrations, but with different drying conditions were compared,
it can be clearly seen that the concentrations of carboxyl end groups of PET in the
PET/HTPB blends without drying are lower than the concentrations of carboxyl end
groups of PET in the PET/HTPB blends with drying. This result indicates that in the twin
screw extrusion without drying esterification reactions consumed more carboxyl end
groups of PET. Extra moisture will facilitate esterification reactions between carboxyl
end group of PET and hydroxyl end group of HTPB.
Figure 5-29: Comparison of carboxyl end group of PET in the low M.W. PET(0.48 IV)/HTPB blends with drying and without drying

Figure 5-30 compares the hydroxyl end groups of PET in the low M.W. PET (0.48 IV) and HTPB blends at two conditions: with pre-drying the PET resins and without pre-drying the PET resins. Figure 5-30 shows that concentration of hydroxyl end group of PET was obviously higher than no reaction scenario which means there exist reactions generating hydroxyl end group of PET. When concentrations of hydroxyl end group of PET in the two PET/HTPB blend samples with the same HTPB concentrations, but with different drying conditions were compared, it can be clearly seen that the concentration of hydroxyl end groups of PET in the PET/HTPB blends without drying are higher than the concentrations of hydroxyl end group of PET in the PET/HTPB blends with drying. The observation of Figure 5-30 agree with that extra moisture will facilitate hydrolysis reactions of PET which will generate more carboxyl and hydroxyl end groups of PET.
Figure 5-30: Comparison of hydroxyl end group of PET in the low M.W. PET(0.48 IV)/HTPB blends with drying and without drying.

Figure 5-31 compares the hydroxyl end group of HTPB in the low M.W. PET (0.48 IV) and HTPB blends at two situations: with pre-drying the PET pellets and without pre-drying the PET pellets. In previous discussions, esterification reactions between PET and HTPB had been confirmed to consume hydroxyl end groups of HTPB. A suspicious hydrolysis reaction of double bond of polybutadiene will generate extra hydroxyl groups to compensate the consumption of hydroxyl groups of polybutadiene during the esterification reaction. The left chart of Figure 5-31, with drying situation, shows this trend. In the right chart of Figure 5-31, the PET pellets were extruded with HTPB but without necessary drying, severe hydrolysis of HTPB can be seen. The hydroxyl group of HTPB was obviously higher than no reaction scenario in all the blends. This comparison clearly confirmed the existence of hydrolysis reaction of HTPB.
Temperature may be one important effect in the reactions between PET and HTPB during reactive extrusion. The low M.W. PET (0.48 IV) with 5 wt% HTPB blends were extruded by twin-screw extruder at three temperatures: 270 °C, 285 °C and 300 °C. Concentrations of hydroxyl end groups of PET, carboxyl end groups of PET and hydroxyl end group of HTPB were analysis by FTIR. Table 5-5 lists concentrations of end groups in the PET/HTPB blends.

Table 5-5: End group concentrations in the low M.W. PET (0.48 IV) with 5 wt% HTPB blends during different extrusion temperatures.

<table>
<thead>
<tr>
<th>Extrusion temperature</th>
<th>OH of PET 10^-6 mol/g</th>
<th>COOH of PET 10^-6 mol/g</th>
<th>OH of HTPB 10^-6 mol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>270 °C</td>
<td>179.0</td>
<td>18.3</td>
<td>96.3</td>
</tr>
<tr>
<td>285 °C</td>
<td>174.8</td>
<td>17.5</td>
<td>98.9</td>
</tr>
<tr>
<td>300 °C</td>
<td>179.7</td>
<td>17.7</td>
<td>97.2</td>
</tr>
</tbody>
</table>

Data in Table 5-5 shows that temperature has no effect on the reactions between PET and HTPB during reactive twin screw extrusion in the 270°C to 300°C temperature range.
5.5 Extration method to confirm reactions between PET and HTPB

To further confirm reactions between PET and HTPB, extraction method was used to physically verify reactions between them. Extraction method is a commonly used physical method to separate materials by their different solubilities in the solvent. PET has very high molecular weight and has very low solubility in chloroform. Hydroxyl terminated polybutadiene (Mn=1200 g/mol), on the contrary, can be totally dissolved in chloroform at room temperature. Extraction experiments were performed on high M.W. PET/HTPB blends. Chloroform was used as the solvent to extract un-reacted HTPB out of PET/HTPB blends. Pellets of PET/HTPB blend were ground into powder to improve extraction efficiency. Extraction experiments were run at room temperature. Every 24 hours the filtration and wash procedure was repeated on the PET/HTPB powder for a total of 96 hours. The final extracted PET/HTPB blend powder was vacuum dried at room temperature to evaporate any residual chloroform.

600 MHZ NMR spectra of extracted PET/HTPB blend powders are obtained. Proton numbers of the C=C olefin group in PET/HTPB blends before and after extraction are calculated by integration of the chemical shifts. Figure 5-32 shows the effect of extraction on C=C olefin group. Similarly, proton numbers of CH\(_2\) methyl group of HTPB in PET/HTPB blends before and after extraction are calculated out. Figure 5-33 shows the effect of extraction on CH\(_2\) methyl group of HTPB.
Firstly, both Figure 5-32 and Figure 5-33 show that after 96 hours of extraction most PET/HTPB blends still have some amount of HTPB. This result indicated that the
reaction between PET and HTPB did occur during extrusion. Reactions between PET and HTPB fixed some HTPB in the PET/HTPB blends even after extraction.

Second, the amounts of C=C olefin groups and methyl groups of HTPB left in extracted PET/HTPB blends are linear with original HTPB concentrations in blends. The reaction degree between PET and HTPB is assumed linear with HTPB concentration in the blends.
Chapter 6

Summary, Conclusions and recommendations

6.1 Summary

The objective of this research is to study the mechanisms and kinetics of the oxidation process for a new copolyester, which is based on unsaturated hydrocarbon modified PET. In this research the unsaturated hydrocarbon is low molecular weight hydroxyl terminated polybutadiene. Amosorb® technology developed by BP Amoco introduced incorporating polybutadiene into PET as an oxygen scavenger. According to the patent, PET with 4-12 wt% polybutadiene and certain amount of cobalt catalyst were blended through twin-screw extrusion. The PET and polybutadiene blend was verified to have low oxygen permeability. Low molecular weight of polybutadiene material was chosen to modify PET. After the modification, the modified PET could keep favorite properties of PET and had an oxygen scavenging capability. The reason for blending hydroxyl terminated polybutadiene (HTPB hereinafter) and PET was that the hydroxyl end groups of HTPB were expected to react with end groups of PET to form a new copolyester. The PET/HTPB copolyester would have different optical, thermal and mechanical properties
than those of a PET/PBD physical blend.

In this research, oxidation mechanisms and kinetics of pure polybutadiene were studied first. Factors like molecular weight and structure configurations of polybutadiene in the oxidation reaction were analyzed. Activation energies of unsaturated olefin groups in the oxidation reactions were obtained.

Then hydroxyl terminated polybutadiene was extruded with PET to form a PET/polybutadiene blend in the twin screw extruder. Oxidation kinetics of PET/polybutadiene blends with different polybutadiene concentrations was obtained. Factors that can affect oxidation kinetics, including the molecular weight of polybutadiene, concentration of polybutadiene and catalyst, were included in the study of oxidation kinetics of this blend.

The reactions between hydroxyl terminated polybutadiene and PET were verified by FTIR end group analysis method, proton NMR method and extraction method. FTIR end group analysis method was used to identify reactions between end groups of PET and HTPB in the reactive extrusion process. Proton NMR method was used to directly confirm the reaction between hydroxyl terminated polybutadiene and PET. Finally a physical method, extraction method, was used to further confirm the reaction between PET and hydroxyl terminated polybutadiene.
6.2 Conclusions

Oxidation mechanism of pure polybutadiene

Based on literature research, the oxidation process of polybutadiene is a free radical reaction. Olefin groups of polybutadiene will combine with oxygen to form free radicals. Peroxyl and alkoxy free radicals are the major forms of free radicals. Peroxides or hydroperoxides are formed during the oxidation reactions as reaction intermediates though quick free-radical termination reactions. The alkoxy free radicals decompose into carbonyl groups, which are the final products of oxidation.

In the mechanism study of pure polybutadiene, an ATR method was used to identify oxidation reactant, oxidation intermediate and products. In the infrared spectra study of oxidation process of polybutadiene, olefin groups, which are the oxidation reactants, were found to decrease; carbonyl groups which are the oxidation products were observed to increase. Similarly, formation and disappearing of oxidation intermediates, peroxides or hydroperoxides, were observed. All observations agree with suggested oxidation mechanisms of polybutadiene.

Oxidation kinetics of pure polybutadiene

The oxidation kinetic study of polybutadiene showed that the oxidation rate of polybutadiene is first order reaction. In the oxidation test of polybutadiene, both the reactants disappearing rate and product formation rate were first order.

Oxidation kinetics of two polybutadiene materials with 1200 g/mol and 2800 g/mol
molecular weights respectively show that low molecular weight polybutadiene has higher oxidation rates than high molecular weight polybutadiene. A proton NMR study of oxidation sequences of olefin double bonds on the polybutadiene molecule showed that olefin double bonds near or at the molecule end were oxidized first and had higher oxidation rates. Low molecular weight polybutadiene has higher amounts of olefin double bonds near molecule ends and has higher oxidation rates than that of high molecular weight polybutadiene.

Polybutadiene has cis, trans and vinyl olefin configurations. Different olefin structures have different oxidation kinetic rates in oxidation reactions. Oxidation kinetics of polybutadiene have been studied at 55°C, 70°C and 100°C and activation energies of three olefin groups of polybutadiene were calculated. Vinyl olefins have the lowest activation energies and highest oxidation rates, trans olefin groups have the medium oxidation rates and cis olefin groups have the lowest oxidation rates.

**Oxidation kinetics of PET/HTPB blends**

PET/HTPB blends were prepared through twin-screw reactive extrusion. PET resins and two hydroxyl terminated polybutadiene materials with different molecular weights (1,200 g/mol and 2,800 g/mol) were extruded in the twin-screw extruder. Oxidation kinetic studies were performed at 40°C, 55°C and 70°C for these PET/HTPB blend samples. ATR spectra of these PET/HTPB blend samples during the oxidation process were obtained. The disappearing rate of olefin double bonds and formation rates of carbonyl groups still followed first order reaction.
**Factors affect oxidation kinetics of PET/HTPB blends**

Kinetic studies of PET/HTPB blends showed that PET/low M.W. HTPB blends have higher oxidation rates than those of PET/high M.W. HTPB blends. This result supports the kinetic study results obtained from pure polybutadiene oxidation indicating that the lower molecular weight polybutadiene has the higher oxidation rate.

Different concentrations of HTPB in the blends have different oxidation rates. Blends with higher polybutadiene concentration have higher oxidation rates.

HTPB dispersion effects in the PET/HTPB blends were studied. Polybutadiene that disperses into smaller particles will have higher surface areas to contact oxygen. Good dispersion of HTPB in PET/HTPB will enhance oxidation kinetics. In reactive twin-screw extrusion of PET/HTPB blends, main screw speed can affect dispersion effect of HTPB in the blends. Three twin screw rotating speeds (200 rpm, 300 rpm, 400 rpm) were used. Oxidation kinetics of the three samples were studied at two temperatures (55°C and 70°C). Experiment results indicate that high twin screw rotating speed will reduce particle size of HTPB in PET/HTPB blend and increase oxidation rate.

Catalyst effects on oxidation kinetics were also studied. PET (0.84 I.V.) is extruded with 5 wt% HTPB (1,200 g/mol) and 100 ppm, 200 ppm, 300 ppm cobalt stearate. ATR spectra studies of oxidation kinetics show that olefin groups decreasing rate are irrelevant with catalyst concentration. However, catalyst was found to decrease oxidation induction time at 40°C oxidation.
Oxidation by-product of PET/HTPB blends

In the GC-MS test, acetaldehyde was identified as major gaseous oxidation by-product which can be released from PET/HTPB blend and pure polybutadiene.

FTIR method to verify reactions between PET and HTPB during reactive extrusion

A Gaussian simulation FTIR method was used to calculate individual end groups in the PET/HTPB blends. This simulation method can analyze reactions between PET and HTPB. This method confirmed that esterification reaction exist between hydroxyl end group of HTPB and carboxyl end group of PET. Hydrolysis reactions of PET or transesterification reactions between PET and HTPB can be the explanation for increasing hydroxyl end groups of PET. The residual oxygen and water generated by esterification reactions between PET and HTPB will promote hydrolysis reaction of HTPB.

Evidence of reaction from Proton NMR

If esterification reactions happens between PET and HTPB, the ester linkage will influence both the chemical shifts of HTPB’s methylene proton and PET’s aromatic proton. 600MHZ proton NMR spectra confirm both two new chemical shifts due to reactions between PET and HTPB.

Extraction Method to confirm reactions between PET and HTPB
PET/HTPB blends were extracted by chloroform for 96 hours. After the extraction, samples were scanned by 600MHZ proton NMR spectra. NMR spectra confirm that all PET/HTPB blends still have some amount of HTPB fixed inside the blends. This result indicates that the reaction between PET and HTPB did happen during extrusion. Reaction fixed HTPB in the PET/HTPB blends even after extraction.
6.3 Recommendations

Low molecular weight polybutadiene has been approved to have strong oxidation capacity due to large amounts of unsaturated olefin groups. Lower molecular weight of polybutadiene has been confirmed to have higher oxidation kinetics when compared with higher molecular weight polybutadiene. As a result, in the research of unsaturated hydrocarbon modified PET as oxygen scavenging system, low molecular weight hydrocarbon should be chose.

Although different configurations of olefin group have different oxidation kinetics in pure polybutadiene, after the high temperature (270°C-280°C) reactive extrusion with PET, only trans- olefin group exists in the blends. As a result, relying on modification of unsaturated hydrocarbon’s configuration to improve oxygen scavenging rate is not a wise approach.

In the research of oxidation by-product in the oxidation reaction of polybutadiene and its blends with PET, acetaldehyde was identified as the major gaseous oxidation by-product which can be released into atmosphere. Although acetaldehyde is not a poisonous substance, great concern will be focused on the oxidation product in packaging, especially in food packaging.

The excellent behavior of polybutadiene as an oxygen scavenger comes from its conjugated olefin groups and large amount of unsaturated olefin groups. Conjugated structure of olefin groups of polybutadiene can provide stability during high temperature
reactive extrusion. The large amount of unsaturated olefin groups provides its oxidation capacity. Actually, there is some other materials can provide same conjugated structures and unsaturated olefin groups. Furthermore, some of these materials are natural products which can erase the safety concern in food packaging. For example, molecules in Figure 6-1 (a), (b) and (c) are pigment materials. All of them can provide conjugated olefin structures and certain amount of olefin groups. Utilizing these kinds of pigment can both increase aesthetic value of packaging product and provide oxygen scavenging capability. Furthermore, lycopene pigment is a natural product from fruits and vegetables which can erase concerns of food packaging safety.

Figure 6-1: Unsaturated pigments
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Appendix A

Peak Quantification Technique in ATR Spectrum of Oxidation of Hydroxyl Terminated Polybutadiene

From Beer-Lambert Law, absorbance is leaner with concentration. For a certain absorbance peak in FTIR spectrum, its value can represent the concentration of a compound in the sample. To observe a peak value change during the HTPB oxidation, different methods were used to quantify a peak value. There are four methods to quantify a peak value. As shown in Figure A-1, peak intensity is the distance from peak zenith to zero absorbance; peak height is the distance from peak zenith to peak baseline; total area is the area below the peak curve; Corrected peak area is the area between peak curve and peak baseline. In the measurement of peak value of a FTIR spectrum, corrected area is commonly used due to the application of baseline correction. In the practical quantification of peak value, peak area usually means the corrected peak area.
Because peak height method cannot be sensitive to peak shape change and can be easily influenced by adjacent peak change, corrected area method is the suitable method of peak quantification in HTPB oxidation.

In the polybutadiene oxidation process, refractive index of the test sample may keep changing during oxidation reaction. Refractive index change will generate “dispersion” effect on peak shapes and locations in ATR spectrum.

According to Beer-Lambert Law

\[ A = \varepsilon \cdot C \cdot d_p \]

Where

\[ A: \text{ absorbity} \]
\[ E \]: molar absorbity coefficient

\[ d_p \]: incident penetrating depth

In ATR spectrum, the penetration depth is also a function of the sample refractive index, so when the refractive index changes, the penetration depth changes as well.

\[
    d_p = \frac{\lambda}{2\pi \sqrt{\sin^2(\theta) - \frac{n^2}{n_r^2}}}
\]

Where

\[ \lambda \]: incident light wavelength

\[ \theta \]: incident light angle

\[ n \]: refractive index of sample

\[ n_r \]: refractive index of prism

Dispersion is the change in the sample’s refractive index as a function of wave number. As it turns out, considerable changes in the peak shape and position can be observed. Dispersion effect can be overcome by the normalization method by internal reference peak. Usually an IR peak of an inert compound, which should keep stable in the oxidation reaction, is picked as internal reference peak. The peak area of this internal reference peak is calculated first. All other peak area is divided by the peak area of this internal reference peak. This normalization step can eliminate dispersion effect in the FTIR spectrum quantification process. In the quantification process of peaks in the FTIR
spectrum of hydroxyl terminated polybutadiene, the peak at 1443 cm⁻¹ was picked as internal reference peak. Peak at 1443 cm⁻¹ is the deformation of CH₃ methyl group which is considered as inert compound during oxidation. All other peak areas are divided by the peak area of 1443 cm⁻¹ methyl group peak. For example, in an ATR spectrum of hydroxyl terminated polybutadiene sample as Figure A-2 shows, base online was drawn from 1435 cm⁻¹ to 1475 cm⁻¹ for CH₃ methyl peak at 1443 cm⁻¹; from 895 cm⁻¹ to 930 cm⁻¹ for vinyl olefin peak at 911 cm⁻¹; from 952 cm⁻¹ to 983 cm⁻¹ for trans olefin peak at 968 cm⁻¹, from 1011 cm⁻¹ to 1109 cm⁻¹ for peroxyl peak at 1049 cm⁻¹; from 1654 cm⁻¹ to 1800 cm⁻¹ for carbonyl peak at 1724 cm⁻¹; from 2963 cm⁻¹ to 3048 cm⁻¹ for cis olefin peak at 3004 cm⁻¹; from 3120 cm⁻¹ to 3670 cm⁻¹ for hydroxyl peak at 3390 cm⁻¹. After base line correction, corrected peak areas of these peaks were calculated in Table A-1, column (a). After obtaining corrected peak areas of each peak, all corrected peak areas were divided by corrected peak area of 1443 cm⁻¹ methyl group in column (a). Results were listed in Table A-1 Column (b). Peak areas in Table A-1 column (b) are the relative peak areas which have been normalized by the reference peak at 1443 cm⁻¹. This normalization step is to minimize the dispersion effect in the quantification process of an ATR spectrum.
<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>Relative peak area after normalized to</td>
</tr>
<tr>
<td></td>
<td>base line correction</td>
<td>1443 cm(^{-1}) reference peak</td>
</tr>
<tr>
<td>(absorbance/cm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1443 cm(^{-1}) methyl peak</td>
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<td>1</td>
</tr>
<tr>
<td>911 cm(^{-1}) vinyl olefin peak</td>
<td>1.7349</td>
<td>2.7154</td>
</tr>
<tr>
<td>968 cm(^{-1}) trans olefin peak</td>
<td>1.4629</td>
<td>2.2897</td>
</tr>
<tr>
<td>1049 cm(^{-1}) peroxyl peak</td>
<td>1.1971</td>
<td>1.8737</td>
</tr>
<tr>
<td>1724 cm(^{-1}) carbonyl peak</td>
<td>5.5916</td>
<td>8.7519</td>
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<tr>
<td>3004 cm(^{-1}) cis olefin peak</td>
<td>0.0539</td>
<td>0.0844</td>
</tr>
<tr>
<td>3390 cm(^{-1}) hydroxyl peak</td>
<td>17.0933</td>
<td>26.7543</td>
</tr>
</tbody>
</table>

Table A-1: Calculation of corrected peak area and relative peak area in ATR spectrum of low M.W. HTPB (Mn=1200 g/mol) at 70°C (oxidation time 15 hours)
Figure A-2: ATR spectrum of hydroxyl terminated polybutadiene
Appendix B

Calibration of Liquid Pump Flow Rate

In the twin-screw extrusion process of PET/HTPB blends, PET resins were feed into the twin-screw extruder by a feed screw and liquid HTPB was injected into the twin-screw extruder by a liquid pump as Figure B-1 shows.

Figure B-1: Experimental setup of twin-screw extrusion of PET/HTPB blend

Concentrations of HTPB in the PET/HTPB blend were primarily controlled by the liquid pump setting. First, the feed rates of PET resin by the feed screw were measured and recorded. The method is: use a bucket to catch all PET resins which were flowing into the
hopper of twin-screw extruder; accumulated weight of PET resins in the bucket was
measured after 30 minutes, e.g., 4.750 kilogram; repeated the measurement process for 3
times and recorded the average feed rate of PET resin; the feed rate of PET resins was
recorded as 9.500 kilogram per hour.

The liquid pump (Model CH-83) was used to inject liquid HTPB into the twin-screw
extruder. This liquid pump is a peristaltic pump (positive displacement pump) usually for
delivering liquid. The liquid is contained in a flexible tube fitted inside the pump casing. A
rotor with three rollers continues compressing the flexible tube. When the rotor rotates,
part of the flexible tube is under compression thus driving the liquid inside the tube
moving along the tube. Figure B-2 shows the design of liquid pump. This liquid pump is
a micro pump which can provide precise flow rate of liquid. However, the control panel
of this liquid pump only provides rotating speed of rotor instead of flow rate of liquid.
Furthermore, for liquids with different viscosity, the flow rates are different even with
same rotating speed of rotor. Flow rates of two HTPB were calibrated before every
twin-screw extrusion process. The calibration procedure is: use an empty bottle to catch all
HTPB liquid injected by liquid pump with different rotating speeds of rotor; recording
accumulated HTPB liquid weight every 30 minutes; draw a flow rate of HTPB versus
rotating speed of rotor as Figure B-3 shows; base on the curve in Figure B-3, find rotating
speed of rotor for desired flow rate of HTPB. For example, for PET/4 wt% HTPB blends,
when feed rate of PET resin is 9.5 kilogram per hour, the flow rate of HTPB should be
396 gram per hour and the rotating speed of liquid pump rotor should be set at 60 cycles
per minute; adjust the rotating speed of liquid pump rotor around 60 cycle per minute until the flow rate of HTPB reaches exactly 396 gram per hour and recorded rotating speed of liquid pump rotor. Before the extrusion of PET/HTPB blends, rotating speed of liquid pump’s rotor should be re-verified to keep precise weight concentrations of HTPB in the PET/HTPB blends.

Figure B-2: Design of liquid pump
Figure B-3: Flow rate of high molecular weight polybutadiene (2800 g/mol) versus rotating speed of rotor of liquid pump (model CH-83)
Appendix C

Oxidation Rate Constants of PET/HTPB Blends

In the study of oxidation kinetics of PET/HTPB blends, ATR spectra were obtained. Figure C-1 shows the ATR Spectra of oxidation process of PET/6wt%HTPB blends at 70°C. Figure C-1(a) is the regional expansion of Figure C-1(b) to clearly observe ATR spectra. The peak at 971 cm\(^{-1}\) is the oxidation reactant, trans-olefin group and the peak at 1713 cm\(^{-1}\) is the oxidation product, carbonyl group. The peak at 971 cm\(^{-1}\) actually represents two chemical bonds, one is trans-olefin group as was shown previously with the section of the pure polybutadiene spectra and the other is antisymmetric C-O stretching of PET molecule. Peaks of these two chemical bonds overlap each other. The C-O structure in the –O–CH\(_2\)–CH\(_2\)–O– section of PET molecule is very stable to resist oxidation. Although the 971 cm\(^{-1}\) peak is the combination of two peaks, C-O stretching and trans-olefin, the decreasing of 971 cm\(^{-1}\) in the oxidation were considered as disappearing of olefin group. The C-O structure of PET molecule has two conformations which are trans conformation and gauche conformation. There was a concern that with long time exposure to high temperature during oxidation, the two conformations of C-O in PET molecule may change. To verify the stability of C-O structure conformation of
PET molecule, peak at 845 cm$^{-1}$ which is trans C-O conformation of PET molecule, peak at 899 cm$^{-1}$ which is gauche C-O conformation of PET molecule and peak at 1340 cm$^{-1}$ which is trans C-O wagging were monitored during the 70°C oxidation experiment of PET/6wt% HTPB blend. Figure C-1 shows the relative peak areas of three peaks of C-O structure of PET molecule change with oxidation time. There were no obvious changes of these three peaks during 10 days oxidation at 70°C. These result indicated that the conformation of C-O structure in PET molecule was stable during oxidation. As a result, the changes of 971 cm$^{-1}$ peaks during oxidation fully represent the disappearing of trans olefin group.
Figure C-1: ATR Spectra of PET/6wt% HTPB blends in the oxidation test at 70°C
Figure C-2: Relative peak area changes with oxidation time at 70°C for PET/6wt% HTPB blend.

In order to eliminate dispersion effect of ATR spectrum, all characteristic peak areas were divided by a reference peak which were described in Appendix 2. In the ATR spectra of oxidation process of PET/HTPB blends, the reference peak is CH\textsubscript{2} methyl group bending in aromatic ring (1408 cm\textsuperscript{-1}) which is supposed to keep stable in the oxidation reaction. After devided by reference peak, [A] represents relative peak area which is a normalization result. In the observation of oxidation reaction of PET/HTPB blends, [A] is the observed relative peak area of ATR spectrum for each component and $[A]_0$ is the initial relative peak area of ATR spectrum for each component before the oxidation reaction start.

Because ATR technology only measures an extreme thin layer on the surface of PET/HTPB blends, oxygen diffusion can be neglected. The oxidation reaction of
PET/HTPB blends can be also treated as pseudo-first-order reaction in the ATR spectrum. A first-order reaction depends on the concentration of polybutadiene in the PET/HTPB blends. Other reactants can be present, e.g. oxygen, but each will be zero-order. The rate law for a first order reaction is:

\[
r = -\frac{d[A]}{dt} = kA
\]

Where \( A \) is the concentration of reactant and \( k \) is the first order rate constant which has units of \( 1/\text{time} \).

The integrated first-order rate law is:

\[
\ln[A] = -kt + \ln[A]_0
\]

In the ATR spectrum of PET/HTPB blends, observed peak area of each characteristic peak represents concentration of component is the test sample.

A plot of \( \ln[A] \) vs. time \( t \) gives a straight line with a slope of \( -k \) which is reaction rate constant. In the pseudo-first order oxidation reactions of polybutadiene in the PET/HTPB blends, the ATR spectra peak areas of each component group are treated as concentrations.

The first-order rate law is transformed as:

\[
\ln \frac{[A]}{[A]_0} = -kt
\]

An example of oxidation rate calculation process is shown as below:

Figure C-3 shows the oxidation process of olefin group (971 cm\(^{-1}\)) in the PET/HTPB
blends at 70°C which is the Figure 4-1 (a) of Chapter 4. In Figure C-2, the trans- olefin peak (971 cm\(^{-1}\)) decreases rapidly in the period of 0 to 3 days and reaches a steady plateau after 3 days. The oxidation of olefin group in the PET/HTPB mainly locates in the time range from 0 to 3 days. Table C-1 shows the change of relative peak areas with time during the oxidation reaction.

![Figure C-3: Oxidation process of olefin group (971 cm\(^{-1}\)) in the PET/HTPB blends at 70°C](image)

Figure C-3: Oxidation process of olefin group (971 cm\(^{-1}\)) in the PET/HTPB blends at 70°C
Table C-1: Relative peak areas of olefin group (971 cm\(^{-1}\)) during the 70°C oxidation of PET/HTPB blends.

<table>
<thead>
<tr>
<th>Oxidation time (day)</th>
<th>Relative peak area of olefin group (971 cm(^{-1}))</th>
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<tbody>
<tr>
<td></td>
<td>PET/ 2wt% HTPB</td>
</tr>
<tr>
<td>0</td>
<td>0.5361</td>
</tr>
<tr>
<td>1</td>
<td>0.4699</td>
</tr>
<tr>
<td>2</td>
<td>0.4316</td>
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<td>3</td>
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</tr>
<tr>
<td>4</td>
<td>0.4261</td>
</tr>
<tr>
<td>5</td>
<td>0.4310</td>
</tr>
<tr>
<td>6</td>
<td>0.4202</td>
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<tr>
<td>10</td>
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</tr>
<tr>
<td>11</td>
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</tr>
<tr>
<td>12</td>
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</tr>
<tr>
<td>13</td>
<td>0.4115</td>
</tr>
<tr>
<td>14</td>
<td>0.4164</td>
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</table>
To obtain oxidation reaction rate of olefin group (971 cm\(^{-1}\)) a plot of \(\ln \frac{[A]}{[A_0]}\) vs. time \(t\) gives a straight line with a slope of \(-k\) which is reaction rate constant. \([A]\) is the relative peak area of 971 cm\(^{-1}\) peak in the oxidation and \([A]_0\) is the relative peak area of 971 cm\(^{-1}\) peak at zero day. For PET/2 wt% HTPB blend, \([A]_0\) is 0.5361; For PET/4 wt% HTPB blend, \([A]_0\) is 0.5723; For PET/4 wt% HTPB blend, \([A]_0\) is 0.7574. For each PET/HTPB blend sample, relative peak area of 971 cm\(^{-1}\) peak was divided by its \([A]_0\) and natural logarithm was applied to obtain \(\ln \frac{[A]}{[A_0]}\) as Table C-2 shows. The oxidation reaction of olefin group in the PET/HTPB blends was considered as occurring in the time range from 0 day to 3 days. Plot of \(\ln \frac{[A]}{[A_0]}\) versus oxidation time from 0 to 3 days is shown in Figure C-4. The slopes in the Figure C-4 are the lose rate of olefin groups in PET/HTPB blends. For PET/ 2wt% HTPB blend, the olefin lose rate is -0.10 per day; For PET/ 4wt% HTPB blend, the olefin lose rate is -0.13 per day; For PET/ 6wt% HTPB blend, the olefin lose rate is -0.16 per day.
Table C-2: Relative peak areas of olefin group (971 cm^{-1}) during the 70°C oxidation of PET/HTPB blends.

<table>
<thead>
<tr>
<th>Oxidation time (day)</th>
<th>PET/ 2wt% HTPB</th>
<th>PET/ 4wt% HTPB</th>
<th>PET/ 6wt% HTPB</th>
</tr>
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<tbody>
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</table>
Figure C-4: Oxidation rate constants at 70°C of olefin groups (971 cm⁻¹) in PET/HTPB blends