Degradation Product Analysis of Bismaleimide Composite

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DEGRADATION PRODUCT ANALYSIS OF BISMALEIMIDE COMPOSITE

A Thesis

Presented to

The Faculty of the Department of Chemistry

Western Kentucky University

Bowling Green, Kentucky

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Wendy Zhong

August 1996
DEGRADATION PRODUCT ANALYSIS OF BISMALEIMIDE COMPOSITE

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ACKNOWLEDGMENTS

I am happy to express my sincere appreciation to Dr. Wei-Ming Lee, whose interest, attitude and aptitude have been of invaluable service to me during my study under his guidance. I would also like to extend my deepest appreciation to Dr. Wei-Ping Pan for his support and guidance. I want to acknowledge the continuing support of Drs. John T. Riley and Thomas K. Green. Also, I would like to thank the faculty and staff in the Department of Chemistry at Western Kentucky University for their encouragement, kind consideration, and excellent teaching during my stay. The graduate assistanship from the Department of Chemistry at Western Kentucky University was also important to complete my study.

Wendy Zhong
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This study evaluates the thermal and oxidative stabilities of a bismaleimide (BMI) polymer composite reinforced with an intermediate modulus graphite fiber, Cytec®5260/IM7. The composite is aged in helium, nitrogen, and air at elevated temperatures up to 600°C. Its weight change is followed thermogravimetrically for stability assessment. The effect of aging gas environment is also studied.

The use of on-line gas cell fourier transform IR spectrometer (FTIR) and mass spectrometer (MS) allows for the identification of decomposition products by evolved gas analysis. This combination of thermogravimetric analysis (TGA) and evolved gas analysis by FTIR and MS yields complementary information regarding pyrolysis and oxidative degradation products. Based on the TGA-FTIR-MS results, the degradation pathways are explored, which may be used for developing new polymer composites having improved stabilities for high temperature aircraft engine applications.
I. INTRODUCTION

The long-term thermal oxidative stability (TOS) of an advanced polymer composite is an important material selection consideration for high speed civil transport (HSCT).\textsuperscript{1} An understanding of the oxidative degradation pathways of the composite can aid the development of polymeric composites having improved TOS for aircraft applications. Bismaleimide/graphite fiber composite, CYTEC 5260/IM7, is a high temperature polymer composite which has been targeted for high speed civil transport application requiring long-term TOS at 177°C (350°F). Because of this unusual lifetime requirements, a need for lifetime prediction exists.

In general, the thermal and oxidative stabilities of a polymer composite are related to the polymer matrix, the reinforcing fiber and the polymer/fiber interface. For a carbon fiber reinforced composite, the thermal oxidative degradation of polymer matrix material usually gives rise to the initial "real" weight loss accompanied by degradation gaseous products. Early moisture and residual volatile losses are not related to a polymer breakdown. Once polymer degradation occurs, it will eventually lead to deterioration of composite properties.\textsuperscript{1} Polyimides are polymers containing cyclic imide groups in the main macromolecular chain. Depending on the moiety structure attached to the imide group, polyimides can be aliphatic, alicyclic, or aromatic and linear or three dimensional structures.\textsuperscript{2} In terms of chemistry, there are two general types of commercial polyimides: thermoplastic polyimides, derived from a condensation reaction between anhydrides or anhydride
derivatives and diamines, and cross-linked polyimides, derived from an addition reaction between unsaturated groups of the preformed imide monomers or oligomers. The imide monomers or oligomers are also derived from the typical condensation reaction to form the imide group, but polymer formation stems from the addition reaction.\(^3\)

Bismaleimides can be converted to homopolymers, copolymers, or terpolymers and used as cross-linking agents. They are of particular interest because of their easy availability, low price, excellent processing characteristics, and outstanding thermomechanical and flammability behavior at elevated temperatures in the final cured state. Resin formulations on the basis of bismaleimides derived from aromatic diamino compounds have been used for castings, for prepregging and glass-fabric laminate fabrication, for filament winding operations together with glass- and carbon-fiber rovings, and recently also as adhesives for metal bondings. The double bonds of the maleimide residues are highly electron-deficient because of the two flanking imide carbonyl groups. They can therefore be polymerized easily by a heat treatment to promote vinyl crosslinking.\(^4\) However, bismaleimide reactions are complex and are less well understood by far.

The graphite fibers are inert to temperature and humidity over the range of most resin service temperatures. Their combination of strength, stiffness, fatigue resistance, density, and toughness is unique in the advanced-composite field. Polycrylonitrile (PAN)-based carbon fibers represent the most important carbon fibers used today. Hercules type IM7, an intermediate modulus and high tensile strength PAN-based carbon fiber, is the continuous reinforcing fiber used in this polymer composite Cytec 5260/IM7. The carbon fiber, due to its better inherent stability, breaks down at higher temperatures (above 600°C).\(^5\)
Numerous thermal analysis techniques have been used to study polymers for research, development and quality control purposes. Specifically, the polymer composite stability is studied by thermogravimetric analysis (TGA) to follow its weight loss from heating. By definition, thermogravimetric (TG) analysis is a thermoanalytical technique where the weight change of a sample is monitored during a dynamic, as well as isothermal, heating program in a specific atmosphere. For some materials, such as polymers, loss of impurities (i.e., residual solvent or starting material) or thermal degradation can be observed as weight losses in a sample during a TG experiment. TG can be used to assess the purity or thermal stability of a polymer and is now a widely used tool in polymer science. It provides information about the sample weight loss due to a programmed temperature rise, as well as the temperature corresponding to a specified weight loss such as 5%, 10%, etc. Two analysis modes are used in this study: a) isothermal thermogravimetry, in which the sample weight loss is followed as a function of time at a constant temperature; b) dynamic thermogravimetry, in which the sample weight loss is measured as the temperature rises. Zhang et al. studied thermal decomposition of the same bismaleimide composite, Cytec 5260/IM7, by using dynamic thermogravimetry methods and found the 5% weight loss temperature occurred between 400-500°C.

TGA experiments carried out using varying heating rates offer a simple and rapid means to a lifetime estimate on the basis of a single reaction order decomposition kinetics. Salin et al. noted, in a carbon fiber reinforced BMI composite, that different activation energies in air depend upon the aging temperature. By using the measured characteristic activation energy, they successfully predicted the weight loss in the temperature range of 300-320°C and 340-380°C for both the neat resin and the composite, respectively.
Several papers have been published on the thermal activation energy for different kinds of polymers. Lee et al.\textsuperscript{1} studied both the diketone-bis-benzocyclobutene (DK-Bis-BCB) neat resin casting and the DK-Bid-BCB/G 30-500 composite using isothermal TGA. Their results indicated that for the first 1-2% weight loss, the composite lost its weight approximately in proportion to aging time suggesting a zero order kinetics. The rate constants obtained for the straight line portion of the 204, 260, and 316°C curves were $5.78 \times 10^9$, $2.67 \times 10^7$ and $5.40 \times 10^6 \text{min}^{-1}$, respectively. The E values obtained for 204-260°C and 260-316°C were 146 and 139 kJ mol\textsuperscript{-1}.

Stenzenberger et al.\textsuperscript{4} investigated thermal decomposition of poly(bismaleimide) by both dynamic and isothermal TGA in nitrogen. Reaction rates and overall activation energies were calculated from isothermal weight loss studies. They assumed that the reaction followed first-order kinetics and the activation energy at product decomposition temperature was 272.57 kJ mol\textsuperscript{-1} for bismaleimides from 460 to 470°C. Thermal degradation kinetics on an aromatic polyimide was carried out under isothermal conditions by Arnold et al.\textsuperscript{8} The aromatic polyimide studied was synthesized from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 2,2'-bis(trifluoromethyl)-4,4'-diamino-biphenyl (PFMB). The decomposition activation energy in air was 210 kJ mole\textsuperscript{-1} and that in nitrogen was 303 kJ mole\textsuperscript{-1}.

Even though TGA is a widely useful tool to study polymer degradations, a limitation to this technique is that it is incapable of identifying the evolved gases from weight losses. Among the various physical methods used for the analyses of thermal degradation products, infrared spectroscopy has often been found very powerful, because it is versatile, rapid, and accessible.\textsuperscript{9} Khorami et al. pursued thermal degradation studies on various organic fiber
materials, combining thermogravimetry (TG) and Fourier transform infrared spectroscopy (FTIR) techniques to simultaneously characterize the thermal behavior and analyze decomposition products. The evolved gases and condensed liquids generated during the thermal decomposition of the materials were respectively collected in an infrared gas cell and on a PVC membrane filter. The gaseous components were analyzed by transmission FTIR, and the condensed liquids were examined directly on the filter by FTIR. They did stepwise thermal degradation studies to establish the minimum temperatures necessary for the evolution of volatiles from these materials.\textsuperscript{9,10}

A TGA interfaced with a Fourier transform infrared spectrometer (FTIR) was also used for identification of small molecules by functionalities by Zhang et al.\textsuperscript{5} In their study, a dynamic thermogravimetry mode was used and a gas cell FTIR analysis showed the gaseous products given off from the same BMI composite to be $\text{CO}_2$, $\text{CO}$, NO, $\text{H}_2\text{O}$, $\text{CH}_4$, phenol and other aliphatic and aromatic hydrocarbons.

Moulinié and his coworkers used TG-FTIR to study the thermal degradation of three types of synthetic thermoplastics: poly(arylene ether)s containing anacenaphthylene moiety, poly(arylene ether ketone)s prepared as analogues of the commercial polymer poly(ether ether ketone) (PEEK), and aromatic polyimides synthesized by a single-step solution polymerization. They revealed that the first weight loss occurring near 147°C corresponded to a slight loss of water (absorbed from atmospheric moisture), while the second, occurring near 315°C, corresponded to a loss of methanol (monitored at 1064 cm$^{-1}$). Moreover, they were able to identify the absorption bands for ammonia, aniline, hydrogen cyanide, isocyanic acid, and phenyl isocyanate. They concluded that both chain scission and ring-opening degradation mechanisms occurred in the polyimides.\textsuperscript{6}
Aust. and others\textsuperscript{11} used the FT-Raman technique to study the polyimide curing reaction. They were able to identify the maleimide C=H bend at 1065 cm$^{-1}$, C=C stretch at 1587 cm$^{-1}$, and the C=O stretch at 1773 cm$^{-1}$ for the polymer. Also they concluded that the alkene groups in the maleimide and succinimide polymer were not lost during the initial "reaction."

In order to gain insight into polymer degradation behavior, mass spectrometry (MS) has been used to study the properties and degradation mechanisms of many common polymeric systems, including several types of polyimides. Stenzenberger et al. carried out pyro-field ion mass spectrometry (PFIMS) to study the thermal degradation of polybismaleimide. They reported that the polybismaleimides with aromatic bridges between the maleimide residues were thermally more stable than those with aliphatic polymethylene sequence, and the aliphatic bridges were thermally less stable than the succinimide rings. They suggested in the spectra of poly(4,4'-bismaleimidodiphenylmethane) and poly(4,4'-bismaleimidodiphenyl ether), succinimide (m/z=99) is only of low intensity and carbon monoxide (m/z=28) is a dominant low molecular weight fraction. Loss of carbon monoxide from the polymer is the consequence of C-N bond cleavage in the maleimide ring.\textsuperscript{4}

TGA and MS measurements are complementary in that the MS can help identify the volatile components lost during the heating cycle, while the TGA gives an accurate measure of total weight loss. Johnson and his coworker\textsuperscript{12} used pyrolysis MS and pyrolysis GC-MS methods to characterize the differences between polyimide films produced by two different curing procedures, 300°C under vacuum and 350°C in a nitrogen atmosphere. Several
pyrolysis products, primarily aromatic hydrocarbon and heterocyclic fragments, were separated and identified by GC-MS.

Redfern and others\textsuperscript{13} used simultaneous TG-DSC and TG-FTIR and TG-MS techniques in studying a range of polymers. The material studied was the powdered phenol formaldehyde/hexamethylene tetramine (hexamine) system. Through evolved gas analysis (EGA), they were able to identify the evolution of water (m/z=18), ammonia (m/z=17), formaldehyde (m/z=29) and phenol (m/z=94) as the most important products.

Arnold et al.\textsuperscript{8} used TG-MS to study the detailed thermal degradation mechanism of BPDA-PFMB films. They reported that the maximum arises from the release of six major products which are CO, HCN, NH\textsubscript{3}, HF, COF\textsubscript{2} and CF\textsubscript{3}H arising from thermal cracking of the diimide and pendant loss.

Jakab and his group studied the thermal decomposition of four aryl-alicyclic polyimides by using thermogravimetry-mass spectrometry and pyrolysis-gas chromatography- mass spectrometry.\textsuperscript{14} In their work, four polyimides based on alicyclic anhydrides and 4,4'-diamino-diphenyloxide were investigated in order to determine the role of the structure of aliphatic segments in the course of thermal degradation. They listed about 18 significant ions, including maleimide (m/z=54 or 97), benzene (m/z=78), analine (m/z=93), benzonitrile (m/z= 103). They explained that there were two peaks for benzene products, the first compound (at 450°C) represented the typical low-temperature products originating from the aliphatic segments. The second one (at 620°C) was released from the functional groups of the polyimides. Water is probably produced from the ether bridges and carbon monoxide from the carbonyl groups of imide cycles. They assumed that the carbon
dioxide is formed by secondary reactions of R-C=O radicals at higher temperatures as follows:

\[
\begin{align*}
R-C=O + H_2O & \rightarrow CO_2 + H_2 + R- \quad (1) \\
R-C=O + R-C-N & \rightarrow CO2 + R-C-N + R
\end{align*}
\]

These reactions were confirmed by the observation that hydrogen and carbon dioxide provided an intensity maximum at similar temperatures (about 600°C). Reaction (2) also explained the formation of cyanide groups which appeared in the form of benzonitrile and HCN in the pyrolyzate. It was likely that high molecular mass products were also released during the decomposition of polyimides, but compounds having low volatility did not reach the mass spectrometer. Therefore, Py-GC was also applied to study the decomposition mechanisms. They were able to identify 26 compounds and established some reaction pathways characteristic of the polyimide samples.

The thermal degradation of a polymer is a complex process. The pathway of thermal degradation depends upon many factors, such as the temperature, the aging time, the purging gas environment, the physico-chemical structure of the material, and the method used are all important factors. Thermal analysis methods can yield a great deal of valuable information about the weight losses occurring at various temperature stages. The combination of a thermogravimetry-Fourier transform infrared spectroscopy (TG-FTIR) and a thermogravimetry- mass spectroscopy (TG-MS) can simultaneously characterize the evolved gas species in the different temperature ranges, and thus be able to understand the thermal characteristics over the programmed temperature range as well as to postulate the possible degradation pathway.
FTIR spectroscopy produces absorptive peaks on an intensity versus wavelength scale, followed by the functionalities of the molecules which are due to vibrational and rotational movement upon absorbing infrared radiation. A mass spectrometer measures ions produced in its ionization chamber and subsequently separated according to their mass-to-charge ratio in the system. Both FTIR and MS are able to simultaneously identify the characteristics of the evolved gas species during the dynamic heating or isothermal aging over a wide range of temperatures. These two techniques are complementary to each other. On the one hand, FTIR can help to separate the same mass species. Mass spectroscopy can identify the diatomic molecules, i.e., oxygen, nitrogen, etc., which have no infrared absorbance. Also, mass spectroscopy is quite precise in identifying the decomposition products produced in a specific temperature region. Therefore, combined TG-FTIR and TG-MS techniques can study weight changes and monitor the species corresponding to these changes under a controlled process.

In this study, the activation energies of CYTEC 5260/IM7 composite in combustion and in pyrolysis are calculated under isothermal conditions to predict the lifetime of the polymer composite. The combination of TG and evolved gas analysis by FTIR and MS yields complementary information regarding pyrolysis and oxidative degradation products. Based on TG-FTIR-MS results, the thermal degradation pathways are explored. Also, the influence of the environment conditions on thermal stability will be discussed. This study will be useful for the development of new polymer composites having improved thermal oxidative stabilities for high temperature aircraft engine applications.
II. EXPERIMENTAL

A. Material

The material investigated is a CYTEC 5260-IM7 composite composed of about 30% by weight of bismaleimide (BMI) resin and 70% by weight of IM7, an intermediate fiber, modulus graphite. A powder sample, which was produced from the composite laminate with a flat drill bit at a speed of 1750 rpm, was utilized for TGA, TGA-FTIR and TGA-MS measurements. Sample powders were not dried before heating. Electronic microscopy (Figure 1) showed the powder sample to be composed of two parts: one being the rod-like carbon fiber; the other part being the BMI polymer adhering to the fiber. The average size is 1-2 μm. The basic chemical structure for BMI is given in Figure 2. BMI monomers polymerize with amines or nucleophilic monomers to form cross-linked, as well as linear long-chain molecules (Figure 3).

B. Thermogravimetric Analyzer

Approximately 10 mg samples were placed in standard aluminum pans and run in a Shimadzu TGA-50. The data were recorded at a scan rate of 180 seconds for 200°C and 60 seconds for 250°C, 300°C and 350°C either in air or nitrogen. TA analysis software was used to plot the weight changes as a function of time. The system followed the weight loss change at a heating rate of 10°C/min to the prescribed isothermal temperatures, such as 200, 250, 300, 350°C, and then held for varying aging times (i.e., 60 hrs, 180 hrs).
Figure 1. Electron microscopy of BMI composite.
Figure 3. Bismaleimide addition-type polyimides: (a) Michael addition BMI (b) bismaleimide-olefin copolymers.
so as to obtain the weight loss over a desired temperature range for degradation activation energy calculations. The gas flow rate was 50 mL/min in air or nitrogen.

C. Thermogravimetric-Fourier Transform Infrared Spectrometry (TG-FTIR) Technique

In order to study the evolved gas products during the composite degradation process, a simultaneous TG-FTIR technique in which a thermogravimetric analyzer is coupled with a Fourier transform infrared spectrometer (FTIR) is used. The TG-FTIR system consists of a modified Perkin Elmer 1650 Fourier Transform Infrared Spectrophotometer (FTIR) interfaced with a DuPont Instruments Model 951 Thermogravimetric Analyzer. Figure 4\textsuperscript{16} shows the schematic diagram of the instrument used in this study. A heated transfer line of 1/8 inch insulated teflon tubing connects the TG quartz tube furnace to a heated 81 cm\textsuperscript{3} FTIR gas cell. A Barnant thermocouple controller maintains the transfer line and gas cell temperature at about 150°C to prevent condensation of the evolved gas products from the TGA. FTIR scans were collected over a wavenumber range of 4000 to 450 \text{ cm}^{-1} at 4 \text{ cm}^{-1} resolution. The average of eight scans, which took 50.1 seconds, was recorded as a file for dynamic TGA runs while 16 scans in 82.2 seconds were used to create the file for isothermal aging runs. The use of Gram/386\textsuperscript{TM} software,\textsuperscript{16} by Galactic Industries Corporation, made FTIR scanning and recording automatic. In this manner, the TG-FTIR system is able to continuously follow the decomposition gaseous products according to their characteristic absorption bands.

The TG-FTIR run conditions employed are as follows:

Approximate sample weight, mg: 20, 100 in air
Figure 4. TG-FTIR schematic diagram.
Approximate sample weight, mg: 20, 30 in He or N₂
Isothermal temperatures, °C: 250, 300, 350, 400, 450
Isothermal aging time, mins: 60, 120
Heating rate, °C/min: 3 and 10.
Purge gas: Nitrogen, Air, Helium
Gas flow rate, mL/min: 50

D. Thermogravimetric-Mass Spectrometry (TG-MS) Technique

The TG-MS system consists of a TA Instruments Model 2950 High Resolution Thermogravimetric Analyzer which is coupled to a Fisons Instruments Model VG Thermolab Mass Spectrometer (Figure 5). A heated glass capillary transfer line is connected to the 170°C inlet port of the mass spectrometer to avoid condensation of evolved gases. It requires 60 milliseconds for gas transfer from the TGA to the MS.

In the experiments, the TG-MS run conditions are as follows:

Approximate sample weight, mg: 10 in Air
Approximate sample weight, mg: 20 in He and N₂
Mass detection range: 1-300 amu
Ionization energy, eV: 30, 70
Heating rate, °C/min: 3 and 10
Gas flow rate, mL/min: 50

The MS system can automatically sample the evolved gas species by mass differences and analyze them with the quadruple analyzer. The mass spectrometer can continuously monitor and store the mass-to-charge intensities of all peaks by using a log histogram mode scan.
Figure 5. TG-MS schematic diagram.
(LHG) during heating. By using the Fisons VG analysis system software, the evolved gas intensity profiles of various species as a function of temperature are obtained. This information can help one to evaluate the stability and the degradation pathways of a polymer composite.
III. RESULTS AND DISCUSSION

A. TGA Results

Samples were run under isothermal conditions using Shimadzu TGA-50 to study the weight losses as a function of time so as to calculate the thermal degradation kinetics. Table 1 summarizes the weight loss changes with isothermal temperature and aging time in both air and nitrogen.

Table 1. Isothermal Weight Loss in Nitrogen and Air

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<tr>
<td></td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>( \text{N}_2/\text{Air} )</td>
</tr>
<tr>
<td>200</td>
<td>0.092 / 0.695</td>
</tr>
<tr>
<td></td>
<td>0.121 / 0.852</td>
</tr>
<tr>
<td></td>
<td>0.309 / 2.136</td>
</tr>
<tr>
<td>250</td>
<td>1.729 / 5.273</td>
</tr>
<tr>
<td></td>
<td>1.785 / 6.154</td>
</tr>
<tr>
<td></td>
<td>----- / -----</td>
</tr>
<tr>
<td>270</td>
<td>2.665 / -----</td>
</tr>
<tr>
<td></td>
<td>2.981 / -----</td>
</tr>
<tr>
<td></td>
<td>----- / -----</td>
</tr>
<tr>
<td>300</td>
<td>4.533 / 15.80</td>
</tr>
<tr>
<td></td>
<td>----- / -----</td>
</tr>
<tr>
<td></td>
<td>----- / -----</td>
</tr>
<tr>
<td>350</td>
<td>9.547 / 25.78</td>
</tr>
<tr>
<td></td>
<td>----- / -----</td>
</tr>
<tr>
<td></td>
<td>----- / -----</td>
</tr>
</tbody>
</table>
Before 200°C, the composite lost very little weight in nitrogen. Even after 48 hours, it only showed a small weight loss of 0.1% (Figure 6). In 180 hours, its weight loss reached 0.3%. Since the total weight loss of water in this composite is about 1%, this weight loss can be considered as the loss of surface water from the composite. Even though the aging time was increased by four-fold from 48 to 180 hours, its weight loss was still less than 1%. It appears that thermal degradation has not yet started. In other words, the composite is quite stable at 200°C in nitrogen. When aged at 270 (Figure 7) and 300°C (Figure 8), in 48 hours, the weight loss of BMI were 2.7 and 4.5%, respectively, which was probably caused by evolution of moisture and volatiles. As the aging temperature was raised to 350°C (Figure 9), the composite showed a 9.5% weight loss in 48 hours.

The weight change in air is much larger than that in nitrogen under the same conditions. For instance, at 250°C (Figure 10) a 5.2% weight loss was seen in air in 48 hours compared to a 1.7% weight loss in nitrogen. In 60 hours, the weight loss in air was increased to 6.1%. But at 300°C (Figure 11), the composite lost 15.8% in air in 48 hours which was about three times that at 250°C. Hence, aging temperature plays a more significant role in the stability of the BMI composite than the aging time. At elevated aging temperatures, the weight loss in air is considerably higher than that in nitrogen. Upon reaching 350°C (Figure 12), a 7% weight loss occurred in air while only 3% occurred in nitrogen. In 48 hours, it lost additional 18.8% in air compared to a 6.5% weight loss in nitrogen because both oxidation and thermal pyrolysis take place in air whereas only thermal degradation occurs in nitrogen. As a result, more weight loss is seen in an air environment. Due to the presence of oxygen in air, CO₂ and H₂O are usually the final products from oxidation. Thus, a polymer composite is less stable in air than in nitrogen, due to additional oxidative degradations.
Figure 10. TGA curve of BMI in air for an isothermal run at 250°C.

Figure 6. TGA curve of BMI in N₂ for an isothermal run at 200°C.
Figure 7. TGA curve of BMI in N₂ for an isothermal run at 270°C.
Figure 8. TGA curve of BMI in N₂ for an isothermal run at 300°C.
Figure 9. TGA curve of BMI in N₂ for an isothermal run at 350°C.
Figure 10. TGA curve of BMI in air for an isothermal run at 250°C.
Figure 11. TGA curve of BMI in air for an isothermal run at 300°C.
Figure 12. TGA curve of BMI in air for an isothermal run at 350°C.
Based on the degradation kinetic expressions suggested by Lee et. al., one can use the following equations to compute the activation energy:

\[
\frac{dw}{dt} = k = Ae^{-\frac{E}{RT}} \tag{3}
\]

\[
w = kt = Ate^{-\frac{E}{RT}} \tag{4}
\]

where \( w \) is the fractional weight loss; \( k \) is the rate constant; \( t \) is the aging time; \( A \) is the frequency factor; \( E \) is the activation energy; \( R \) is the gas constant; and \( T \) is the aging temperature.

The thermal degradation activation energies in nitrogen and air are summarized in Tables 2 and 3, respectively.

| Table 2. Thermal Decomposition Kinetics of BMI Composite in \( \text{N}_2 \) |
|---------------------------------|-----------------|-----------------|------------------|
| \( k, \text{sec}^{-1} \) | \( k_1(T_1, \text{K}) \) | \( k_2(T_2, \text{K}) \) | \( E \) |
| Temperature | | | |
| 200 - 250°C | \( 9.28 \times 10^{-10} \) (473) | \( 9.57 \times 10^{-9} \) (523) | 96 |
| 250 - 300°C | \( 9.57 \times 10^{-9} \) (523) | \( 5.14 \times 10^{-8} \) (573) | 84 |
| 300 - 350°C | \( 5.14 \times 10^{-8} \) (573) | \( 6.81 \times 10^{-8} \) (623) | 16 |

From Table 2, one can see that the activation energies in nitrogen at the low temperatures, such as 200, 250°C, were very high. In other words, it was not a thermodynamically favorable process. When the temperature increased from 250 to 300°C, the activation energy decreased slightly, which meant, in this temperature region, thermal degradation was more likely to occur. However, the activation energy is still very high. As the temperature rose
to 350°C, the activation energy became fairly low, which indicated that this temperature was quite favorable for decomposition to occur.

Table 3. Thermal Decomposition Kinetics Data for BMI Composites in Air

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( k_1(T_1,K) )</th>
<th>( k_2(T_2,K) )</th>
<th>( E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 - 250°C</td>
<td>( 1.11 \times 10^8 ) (473)</td>
<td>( 8.35 \times 10^8 ) (523)</td>
<td>83</td>
</tr>
<tr>
<td>250 - 300°C</td>
<td>( 8.35 \times 10^8 ) (523)</td>
<td>( 1.21 \times 10^7 ) (573)</td>
<td>19</td>
</tr>
<tr>
<td>300 - 350°C</td>
<td>( 1.21 \times 10^7 ) (573)</td>
<td>( 3.04 \times 10^7 ) (623)</td>
<td>55</td>
</tr>
</tbody>
</table>

In Table 3, the activation energy in air between 200 and 250°C was found to be 83 kJ/mole, slightly lower than the corresponding 96 kJ/mole in nitrogen. But, between 250 and 300°C, the activation energy in air at 19 kJ/mole was very low. It seemed reasonable because it showed that decomposition in air had started. However, the activation energy in air obtained for the 300 to 350°C range was found to be, unexpectedly, larger than that from 250 to 300°C. This reversed trend can be explained by two possible reasons:

1. Polymer weight concentration effect. Due to the relatively high aging temperature (300 - 350°C range), considerable weight loss has occurred. As a consequence, the polymer fraction remaining in the composite is diminishing causing a limitation to the oxidative degradation reactions in air. The higher the aging temperature, the greater this polymer concentration effect becomes.
2. Order of the degradation kinetics. Zero order kinetics had been employed for the activation energy computation. According to Lee et al.,\(^1\) the composite weight loss rate is independent of the degradation kinetic order only when the sample weight loss is within the first 1-2%. At 250°C, the sample weight losses in air (4.9% in 48 hrs and 5.4% in 60 hrs) had exceeded this 1-2% weight loss limit. Thus, first order kinetics may need to be considered.

To estimate the service time for a 1% weight loss at 177°C in air, one can solve for time in equation (4) using the 177°C rate constant extrapolated from the 200-250°C activation energy. The estimated service time is 733 hours. It should be pointed out that the actual service time may be much longer. A possible reason is that the aging experiment is not long enough. In other words, the sample weight loss has not reached the zero order steady state. At the steady state, the \(k_{200°C}\) value should be smaller, thereby giving rise to a smaller \(k_{177°C}\) and producing a larger lifetime. Moreover, a powder sample was used in this experiment. Comparing to a composite panel, the much smaller powder sample is easily penetrable to air, which greatly speeds up the oxidative degradation process. Therefore, the lifetime in a panel is lengthened due to slow air diffusion and subsequent oxidative decomposition. Thus, the lifetime for 1% weight loss at 177°C would be longer than the calculated 733 hours.

B. TGA-FTIR Results

1. TGA

When heated from room temperature to 1000°C at 10°C/min in air, the BMI composite started to lose weight above 300°C (Figure 13). The composite weight loss
derivative curve typically displayed three peaks. They are at 411, 555 and 649°C corresponding to 6, 26 and 70% weight losses, respectively. The third peak at about 70% weight loss is associated not only with the continuing polymer degradation process but also with carbon fiber degradations. When heated to 600°C at 10°C/min, the composite only lost about 0.5% weight of its surface moisture before 100°C in nitrogen (Figure 14), helium (Figure 15) or air (Figure 16). However, in nitrogen and helium, the composite displayed only one weight loss rate peak at about 430°C, instead of the two at 417 and 563°C, as noted discrepancy of the result obtained in air. These TGA results are similar to previously reported data.\textsuperscript{5}

The composite was then heated to several aging temperatures (250, 300, 350, 400°C) and kept for a prescribed aging time (120 min) to study its weight loss under isothermal conditions. Their weight changes are listed in the table below. In addition, the weight loss at 450°C for 60 minutes is also tabulated in the following table:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Time</th>
<th>% Wt. Loss (Air)</th>
<th>% Wt. Loss (He)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250°C</td>
<td>120 min</td>
<td>0.81%</td>
<td>1.01%</td>
</tr>
<tr>
<td>300°C</td>
<td>120 min</td>
<td>3.24%</td>
<td>2.95%</td>
</tr>
<tr>
<td>350°C</td>
<td>120 min</td>
<td>9.60%</td>
<td>4.98%</td>
</tr>
<tr>
<td>400°C</td>
<td>120 min</td>
<td>16.93%</td>
<td>11.95%</td>
</tr>
<tr>
<td>450°C</td>
<td>60 min</td>
<td>21.29%</td>
<td>12.00%</td>
</tr>
</tbody>
</table>
Figure 13. TG-DTG curve of BMI heated in air up to 1000°C.
Figure 14. TG-DTG curve of BMI heated in N$_2$ up to 600°C.
Figure 15. TG-DTG curve of BMI in He heated up to 600°C.
Figure 16. TG-DTG curve of BMI heated in air up to 600°C.
Figure 17 is the plot of weight loss versus aging time under isothermal conditions in air. When a composite is held at 250°C for 120 min, its weight loss in air is only 0.81%, which is probably just surface water loss. Thus, the composite having only a weight loss less than 1% is stable. When the aging temperature was raised to 300°C, the sample weight loss increased by more than three times (3.24%) compared to that at 250°C. In addition to surface water loss, the BMI composite starts to degrade at this temperature, which is confirmed by FTIR data to be discussed later. At 350°C the sample weight loss was again about three times (9.60%) of that at 300°C, thus showing that the weight loss data follows a trend close to an exponential dependence on aging temperature up to 350°C. Beyond 350°C, the rate of weight loss with temperature decreased slightly while the total weight loss continued to increase, which is indicative of the initiation of additional degradation pathways at elevated temperatures.

In helium, the weight losses were similar to those in air up to 350°C. Above 350°C, the weight losses in helium were smaller than those in air (Figure 18). Thus, the BMI composite is more stable in helium, an inert environment, than in air, a combustible environment. Since only thermal degradation can occur in helium, it is less detrimental to the composite than in air where both thermal and oxidative degradation take place. It is also the reason that in nitrogen and helium, only one weight loss rate peak occurred while two occurred in air. Consequently, the composite lost more weight in air than in helium.

2. Blank FTIR Runs

Blank FTIR calibrations were run in air (Figure 19), nitrogen (Figure 20), and helium (Figure 21) at 20°C/min to compare the effect of purging gas environment. In these figures,
Figure 17. TG curve of BMI in air under isothermal conditions.
Figure 18. TG curve of BMI heated in air and helium at 350°C.
Figure 19. Blank FTIR calibration in air.
Figure 20. Blank FTIR calibration in N₂.

Absorbance / Wavenumber (cm⁻¹)
Figure 21. Blank FTIR calibration in He.
the horizontal axis represents wavenumbers, (cm\(^{-1}\)) while the vertical axis is the IR intensity in absorbance units. In air, both CO\(_2\) (2358 cm\(^{-1}\)) and H\(_2\)O (1683 cm\(^{-1}\)) were monitored. Water was seen in N\(_2\) and neither water nor CO\(_2\) was observed in helium. In addition to the presence of water and CO\(_2\) peaks, the intensity of these peaks increased with rising temperature up to 600°C. But by comparison, their intensities were less than those in the presence of the BMI composite sample. For instance, the ratio for water intensity was 1:2 (Table 5)

<table>
<thead>
<tr>
<th>Purging Gas</th>
<th>CO(_2)</th>
<th>H(_2)O</th>
<th>IR Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>+</td>
<td>+</td>
<td>increases with temperature</td>
</tr>
<tr>
<td>N(_2)</td>
<td>-</td>
<td>+</td>
<td>increases with temperature</td>
</tr>
<tr>
<td>He</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

+ observable; - not-observable.

3. **The Effect of Aging Environment**

Figure 22 shows the three-dimensional FTIR spectra of BMI composite decomposition products at 10°C/min in air. In these three dimensional plots, the horizontal axis and vertical axis give the wavenumbers in cm\(^{-1}\) and IR intensity in absorbance units, respectively, whereas the third axis represents heating time in seconds which is equivalent to temperature for a constant heating rate run. The FTIR scans started at room temperature (25°C) and finished at 600 °C. The average of 8 consecutive FTIR scans, which takes 50
Figure 22. 3D FTIR spectra of gases from BMI heated in air at 100°C/min.
seconds, is put into a file for display. For example, the sample temperature at file number 20 was 192°C, which was calculated from the equation below:

\[
\text{Temperature, } ^\circ\text{C} = \text{File Number} \times \frac{50 \text{ sec/file}}{60 \text{ sec/min}} \times 10^\circ\text{C/min} + 25
\]

For the long isothermal aging runs 16 continuous scans, which took 82 seconds, were grouped together to reduce the data storage requirement. For example, the 120 minute 300°C isothermal run started the heating to 300°C at 10°C/min and the sample was held for 120 min. upon reaching the target temperature. In this case, it took 21 files to reach 300°C, and the FTIR data after 25.6 min. into 300°C were stored in file number 40.

In air, CO\textsubscript{2}, CO and H\textsubscript{2}O are the main evolved species, along with a small amount of organic functional groups such as -C=O. Most of these evolved gases were seen at about 430 and 580°C, similar to the FTIR results by Zhang.\textsuperscript{5} Only a few organic compounds were observed in air, probably due to the presence of oxygen which tends to oxidize the organics into CO\textsubscript{2} and H\textsubscript{2}O in a combustion environment. The formation of CO during the thermal oxidative degradation arose from the scission of the amide ring and decarboxylation.

On the other hand, CO\textsubscript{2}, CO and water (similar to that in air) were also given off in He and N\textsubscript{2} but to a lesser extent. Figure 23 shows a comparison of CO\textsubscript{2} evolution in air and in helium. In addition, a large amount of organic species such as CH\textsubscript{4} (3016 cm\textsuperscript{-1}), aromatic, aliphatic C-H stretching (3060-2880 cm\textsuperscript{-1}), carbonyl C=O groups (1710 cm\textsuperscript{-1}) which may overlap with the water peaks, aromatic ring C=C vibrations (1500, 1600 cm\textsuperscript{-1}), symmetrical bending (-CH\textsubscript{3}) and asymmetrical bending (-CH\textsubscript{3}) (1400 cm\textsuperscript{-1}), C-H bending (1100 cm\textsuperscript{-1}), O-H bending (1300 cm\textsuperscript{-1}), aromatic C-H out of plane bending (720 cm\textsuperscript{-1}) were observed
Figure 23. A comparison of CO\textsubscript{2} evolution in air and helium.
These functional groups were observed by mass spectroscopy as well, which will be discussed later. By comparing the BMI FTIR spectra with standards, toluene was found. Its characteristic wavenumbers are 690, 730, 1100, 1500, 1700 and 2800-3200 cm\(^{-1}\).

Another characteristic group identified in the spectra was carbonyl -C=O at 1715 cm\(^{-1}\). Its release profile was plotted and is illustrated in Figure 25. One can observe that it started to evolve at about 380°C and its absorbance intensity increased gradually with temperature. At about 500°C, it reached its maximum value and remained flat as the temperature was increased to 600°C. By looking at the BMI monomer structure, one can see the existence of carbonyl -C=O in the succinimide rings, which was detected by FTIR. These structures were also confirmed by MS data to be discussed later. However, there was no significant difference between aging in N\(_2\) and He except for the presence of a small amount of water in the nitrogen purge gas.

4. Heating Rate Effect

Figures 22 and 26 show the three-dimensional (3D) FTIR profiles for the 10°C/min (fast) and 3°C/min (slow) heating rates in air, respectively. At 3°C/min, the CO\(_2\) peak at 2358 cm\(^{-1}\) displayed a shoulder at about 450°C. These results were indicative of two kinds of mechanisms for CO\(_2\) formation at the slow heating rate. However, at 10°C/min, the shoulder was not obvious due to the overlapping of these two mechanisms.

Figures 27 and 28 are the 3D FTIR profiles for the 10°C/min (fast) and 3°C/min (slow) heating rates in He, respectively. Little difference between the two was seen. However, there was a shift of base line in the fast (10°C/min) heating rate (Figure 27)
Figure 2.4. Some characteristic peaks of gases released during the heating of BMI in N₂.
Figure 25. Carbonyl $-\text{C}=\text{O}$ absorbance profile in helium.
Figure 26. 3D FTIR spectra of gases from heating BMI in air at 3°C/min.
Figure 27. 3D FTIR spectra of gases from heating BMI in helium at 10°C.
Figure 28. 3D FTIR spectra of gases from heating BMI in helium at 3°C/min.
between \( Z = 2300 \) (400°C) and \( Z = 3100 \) (550°C) while it was not obvious in Figure 28. This shift was due to the formation of a large amount of particulates in the form of aerosol in the TGA furnace, which were carried into the gas cell, causing light scattering, and raised the base line. At the slow heating rate, these species were formed slowly so this phenomenon was not observed.

5. **Aging Temperature Effect**

*In Air.* At 250°C (Figure 29), no obvious evolved gaseous products were observed by FTIR but one can see a small “bump” at 2100 cm\(^{-1}\) after it reached 250°C and continued to the end of the experiment. This observation was confirmed by the TGA results where no weight loss was noted before 300°C, except for a small amount of water given off from the surface of the composite. At 300°C (Figure 30), one can see that a very small amount of CO\(_2\), CO and water started to evolve from the sample and continued to the end of the run, indicating that the composite started to degrade at 300°C and the first degradation products were CO\(_2\) and CO (except for surface water). Thus, composite was stable to 300°C. At 350 (Figure 31), 400 (Figure 32) and 450°C (Figure 33) increasingly larger amounts of organic compounds were evolved, starting at about \( Z = 2000 \) (T = 293°C) and ended at approximately \( Z = 2037 \), which signaled the end of isothermal aging stage. It involved two stages: 1) dynamic heating at 10°C/min to the designated temperature; 2) 120 minutes hold at that temperature. For instance, for the 350°C isothermal run, the sample started to evolve, when heated to 295°C, species such as CO\(_2\), CO, H\(_2\)O and some organic species (1200-1700 cm\(^{-1}\)) etc. The organic species were observed from 295 to 350°C. These species were still present
Figure 29. 3D FTIR spectra of gases from heating BMI in air during an isothermal 250°C run.
Figure 30. 3D FTIR spectra of gases from heating gBMI in air during an isothermal 300°C run.
Figure 31. 3D FTIR spectra of gases from heating BMI in air during an isothermal 350°C run.
Figure 32. 3D FTIR spectra of gases from heating BMI in air during an isothermal 400°C run.
Figure 33. 3D FTIR spectra of gases from heating BMI in air during an isothermal 450°C run.

Absorbance / Wavenumber (cm⁻¹)
in the first 18 minutes of the isothermal stage. However, they were absent after this first 18 minutes. In addition, the amount of absorbance reached its maximum at the target temperature (350°C in this case) and diminished with elapsed time. In this region, some of the peaks overlapped with the water absorption bank.

**In Helium.** At 250°C (Figure 34), no gaseous products were detected by FTIR just like that in air. At 300°C (Figure 35), one began seeing a small amount of organic compounds evolve in the wavenumber range of 1400 and 1800 cm⁻¹, but without CO₂ and CO. At 350°C (Figure 36), a larger amount of CO was produced. At 400 (Figure 37) and 450°C (Figure 38), increasingly larger amounts of organic compounds were evolved in the as observed in region of 1000-1800 cm⁻¹. However, the CO and CO₂ quantities were much less than those in air. The identification of these by FTIR alone was difficult and another analytical technique mass spectroscopy, was employed, as is discussed in the next section.

C. **TG-MS Results**

1. **TGA**

When heated from ambient temperature to 600°C at 10°C/min in air (Figure 16), the BMI composite started to lose weight around 300°C. It displayed two major weight loss rate peaks. They were at 416 and 563°C corresponding to 7 and 28% weight losses, respectively. When heated to 600°C at 3°C/min (Figure 39), its weight loss peaks occurred at slightly different temperatures, namely 394 and 534°C. They were approximately 20 to 30°C earlier than those occurring at 10°C/min. However, there was little difference in their actual weight loss. The composite displayed only one 7% weight loss peak at 425°C in helium at 10°C/min (Figure 15). While heating the composite at 3°C/min (Figure 40) gave rise to similar weight
Figure 29. 3D FTIR spectra of gases from heating BMI in air during an isothermal 250°C run.

Figure 34. 3D FTIR spectra of gases from heating BMI in He during an isothermal 250°C run.
Figure 35. 3D FTIR spectra of gases from heating BMI in He during an isothermal 300°C run.
Figure 37. 3D FTIR spectra of gases from heating BMI in He during an isothermal 400°C run.
Figure 38. 3D FTIR spectra of gases from heating BMI in He during an isothermal 450°C run.
Figure 39. TG-DTG curve of BMI heated in air at $3^\circ$C/min.
Figure 40. TG-DTG curve of BMI heated in He at 3 °C/min.

Weight (%)
loss at 415°C which is 10°C earlier than that at 10°C/min. These data agreed with the TGA-FTIR data in the previous section.

2. Mass Spectrometry (MS)

**70 eV Ionization.** The MS results for the 10°C/min combustion of BMI composite in air were presented in Figure 41. It included the evolution of CO$_2$ (m/z=44) and H$_2$O (m/z= 18) from ambient temperature to 1000°C. However, the larger molecules, i.e., benzene and its derivatives, were not observed in the MS data. It was easy to find that the CO$_2$ absorbance peak is quite similar to the DTG curve. From this curve, one can see the CO$_2$ started to evolve around 300 and at 350°C, it reached the first maximum. These peaks were probably related to the scission of the weaker bonds in the composite. At 550°C, the second peak appeared, which has a higher absorption intensity than the first one. It is most probably related to the breakdown of the BMI resin. Finally at 650°C, a sharp increase in CO$_2$ production occurred representing the continuing decomposition of BMI resin as well as the onset of carbon fiber decomposition.

At the same time as CO$_2$, H$_2$O was released. It showed four absorption peaks. The first one, below 100°C, was due to the evolution of surface moisture. The second one at 350°C, was probably related to the moisture absorbed in the composite, or it might be formed by the scissions of the weaker bonds and then, oxidation products from the oxygen in air. The third and fourth at 550 and 650°C were believed to be produced by the degradation or hydrolysis reaction of the BMI resin. It was evident that H$_2$O and CO$_2$ were the two main degradation products in this case. This observation was also found in the FTIR results discussed in the previous section.
Figure 41. Profiles of some masses from room temperature to 1000°C in air.
At 70eV, the major decomposition products of combustion were H\textsubscript{2}O and CO\textsubscript{2}. The organic species were not detected because of two major factors:

1. There is sufficient oxygen in air to complete oxidation and to form stable final products - CO\textsubscript{2} and H\textsubscript{2}O from organic carbon and hydrogen.

2. This ionization energy (70 eV) is high enough to break the organic species into smaller ions so that large organic species are not detected by MS.

30 eV Ionization. At 30eV, organic species were also not observed by MS during aging of the sample in air. Hence, no organic component was detected in the presence of oxygen in air by mass spectrometry either at 30eV or 70eV.

On the other hand, the composite only went through thermal pyrolysis in He. It was decomposed into small fragments with increasing temperature. Because of the absence of oxygen in He, these fragments can not react with oxygen to form H\textsubscript{2}O and CO\textsubscript{2} and, thus, stay in the fragments’ form which was detected by the mass spectrometer. Consequently, large organic species became observable by MS. For example, fragments associated with C\textsubscript{6}H\textsubscript{6} (m/z=78), C\textsubscript{6}H\textsubscript{5}N or toluene (m/z=92), phenyl isocyanate (m/z=118), methyl phenyl isocyanate (m/z 131) and benzosuccinimide (m/z=174) were collected by MS (Figure 42).

To probe possible degradation pathways, the mass-to-charge (m/z) data were followed as a function of temperature. A given mass was plotted with increasing temperature as a mass profile to follow its change from decomposition. What one wishes to know is when -- i.e., at what temperature -- a given species is noted suggesting the initiation of a degradation pathway, if and when this mass species develops into a maximum, and when it diminishes to a minimum. Sometimes, several different mass profiles would show similar trends with changing temperature because of common degradation pathways.
Figure 42. A typical mass spectrum of gases from heating BMI in He.
Table 6 lists the major fragments detected by the mass spectrometer and the temperature ranges of the pyrolysis products in He to 600°C at a 10°C/min heating rate. From the table, one can see that all the peaks fell into two temperature ranges: one at 410-450°C, and the other at 550-580°C. Similar results were noted by the TGA weight loss data. Figures 43, 44 and 45 displayed the mass profiles of a few important fragments.

3. Proposed Degradation Pathways

The formation of benzosuccinimide (m/e 174) fragment II is the evidence of the bismaleimide breakdown at C-phenyl rather than N-phenyl position. If it were to cleave at the N-phenyl position, both maleimide (m/z 97) and succinimide (m/z 99) would have been observed. Since they were not noted, the bismaleimide breakdown did not take place at this location.

Scheme 1

Another product from scheme 1 was methylphenylsuccinimide (m/z 188) free radical I. However, it was not be detected by MS possibly due to its low volatility and/or short lifetime in the free radical form.

Scheme 2
<table>
<thead>
<tr>
<th>M/e</th>
<th>Products</th>
<th>Ti (°C)</th>
<th>Tmax₁ (°C)</th>
<th>Tmax₂ (°C)</th>
<th>Tᶠ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>174</td>
<td>benzosuccinimide</td>
<td>410</td>
<td>440</td>
<td>---</td>
<td>510</td>
</tr>
<tr>
<td>160(159)</td>
<td>C₇H₆N(CO)₂</td>
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<td>430</td>
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<td>380</td>
<td>420</td>
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<td>370</td>
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<td>---</td>
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<tr>
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<tr>
<td>103</td>
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<tr>
<td>92</td>
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<td>560</td>
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<tr>
<td>91</td>
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<td>420</td>
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<tr>
<td>89</td>
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<tr>
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<tr>
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<td>---</td>
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<tr>
<td>65</td>
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<tr>
<td>52</td>
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<td>570</td>
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<tr>
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<td>C₄H₃</td>
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<td>580</td>
<td>600</td>
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<td>390</td>
<td>500</td>
<td>570</td>
<td>600</td>
</tr>
</tbody>
</table>

T₁ is the initial absorption temperature;  
Tmax₁ is the temperature of the first maximum absorption;  
Tmax₂ is the temperature of the second maximum absorption;  
Tᶠ is the final absorption temperature.
Figure 43. Profiles of some masses from BMI pyrolysis.
Figure 44. Profiles of some masses from BMI pyrolysis.
Figure 45. Profiles of some masses from BMI pyrolysis.
Scheme 2 postulates the breakdown of the succinimide ring to form methylphenyl isocyanate III (m/z 132) by giving off CO and a C\textsubscript{2} fraction. The methylphenyl isocyanate (m/z = 132) was found in the same temperature range as product II.

Scheme 3

\[
\text{Scheme 3}\n
\text{III (m/z=132, 131) } \xrightarrow{\text{CO}} \text{ IV (m/z=103)}
\]

Scheme 3 theorizes the formation of fragment IV by carbon monoxide abstraction.

Scheme 4

\[
\text{Scheme 4}\n
\text{IV (m/z=103) } \xrightarrow{\text{N}} \text{ V (m/z=89, 90)}
\]

Scheme 4 shows the denitrogenation to produce species V. This gave a small amount of product V(m/z 89). However, it was not a stable form so that it may undergo mono-, di-, tri-protonation reactions to form toluene (m/z 91) etc., which was detected by MS and FTIR.

Scheme 5

\[
\text{Scheme 5}\n
\text{II (m/z=174) } \xrightarrow{\text{CH}_3 \text{ or CH}_2} \text{ VI (m/z=159, 160)}
\]

Product VI (m/z 160) was present in the MS data. It was assumed to have come from the ring opening of succinimide II and the subsequent loss of methylene or methyl group.

Scheme 6

\[
\text{Scheme 6}\n
\text{VI (m/z=159, 160) } \xrightarrow{\text{CH}} \text{ VII (m/z=146, 145)}
\]

Scheme 6 involves the cleavage of -CH group giving rise to the formation of product VII (m/e 146) with the loss of the methine ion.
Scheme 7

\[
\begin{array}{c}
\text{VII (m/z=146, 145)} \quad \rightarrow \\
\text{VIII (m/e=118)}
\end{array}
\]

Scheme 8

\[
\begin{array}{c}
\text{VIII (m/e=118)} \quad \rightarrow \\
\text{IX (m/z=90, 92)}
\end{array}
\]

Scheme 7 postulates the loss of CO from the isocyanate side chain from the fragment VII and scheme 8 assumed the loss of additional CO from species VIII.

Scheme 9

\[
\begin{array}{c}
\text{IX (m/z=90, 92)} \quad \rightarrow \\
\text{X (m/e=78, 77)}
\end{array}
\]

Scheme 10

\[
\begin{array}{c}
\text{V (m/z=89, 90)} \quad \rightarrow \\
\text{X (m/e=78, 77)}
\end{array}
\]

A large amount of benzene was detected by MS. It displayed two peaks suggesting the possibility of its formation from two sources. Scheme 9 suggests the loss of nitrogen from fragment IX and scheme 10 represents its formation from the product V by the loss of -CH group. The possible mechanisms were proposed in the following Figure 46.
Figure 46. Mechanism of BMI degradation pathways.
IV. CONCLUSIONS

Thermal analysis of the composite Cytec 5260/IM7 indicated that the composite was stable to 250°C in air, helium and nitrogen. It was more stable in an inert environment, i.e., nitrogen and helium, than in air. In helium or nitrogen, there was only one pyrolysis weight loss rate peak noted, while in air, there were two peaks which suggested the occurrence of pyrolysis as well as oxidative decomposition. The isothermal weight loss studies resulted in a calculated activation energy of 80 kJ mol\(^{-1}\) from 200 to 250°C. Degradation kinetics predicts the composite to have a 733-hour life-time at 177°C in air if powder form was used. In nitrogen, it has a higher activation energy at 96 kJ mol\(^{-1}\), and would have a longer lifetime than in air.

Both TG-FTIR and TG-MS combined techniques identified CO, CO\(_2\), H\(_2\)O and other large organic molecules as the evolved gases from aging. In helium and nitrogen, FTIR showed the presence of CO\(_2\), CO, and H\(_2\)O above 300°C, whereas in air, they were detected 50°C earlier. Large amounts of organic species were observed in an inert gas environment. They are typically in the regions of 1200-1700 cm\(^{-1}\) and 2800-3100 cm\(^{-1}\). However, very little was seen in air, a combustible environment, except for CO\(_2\) and H\(_2\)O.

On the basis of TG-FTIR and TG-MS studies, the initial decomposition in inert environment appears to be cleavage of C-phenyl segments at the aliphatic carbon site which is known to be less stable than the aromatics. It is followed by the breakdown of succinimide rings which eventually leads to the formation of a large amount of small organics such as...
benzene (m/z = 78), toluene (m/z = 91) or amine (m/z = 91), phenyl isocyanate (m/z 118), methylphenyl isocyanate (m/z 131) benzosuccinimide (m/z 174), which were collected by MS. Unfortunately, little information is obtainable for oxidative decompositions due to the formation of CO₂ and H₂O during combustion.

Even though the proposed degradation pathways from this study offer a fairly reasonable explanation of the experimental data, the actual degradation processes which may involve other reactions such as hydrogen-transfer, rearrangement, hydrolysis, etc., are very complex. In order to further understand them, other analytical techniques such as spin resonance spectroscopy, GC-MS, etc., and a combination of these techniques may be required.
V. BIBLIOGRAPHY


15. Yang, X.D. SEM, Western Kentucky University, **1996**.
