Characterizing the Ductile-Brittle Transition of Polyamide-11 / Purification and Characterization of Boron Nitride Nanotubes

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Characterizing the Ductile-Brittle Transition of Polyamide-11 / Purification and Characterization of Boron Nitride Nanotubes

A thesis submitted in partial fulfillment of the requirement for the degree of Bachelor of Science in Chemistry from The College of William and Mary

by

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Accepted for

(Honors, High Honors, Highest Honors)

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Abstract

Semi-crystalline polymers undergo a transition from ductile to brittle behavior that has traditionally been characterized by the molecular weight (M_w). However, using M_w as a determinant of the ductile brittle transition has been proven to be imprecise. To better understand the ductile-brittle transition, polyamide-11 (PA-11) was degraded in water and low molecular weight acids: acetic and butanoic. The M_w of PA-11 degraded 4 times faster in acetic and 8 times faster in butanoic acid than when aged in water. This accelerated aging technique separated the role of crystallinity from a changing molecular weight on ductility. This research shows that crystallinity determines the ductile-brittle transition, not the molecular weight.

To determine the primary mechanism that causes crystallinity to increase during degradation samples of differing molecular weight were aged in argon. This environment is absent of a degradative species. It tests if polymer chains can rearrange into crystalline regions using only thermal energy, a process called thermal annealing. This research showed that chemicrystallization, not thermal annealing, is the reason for the increase in crystallinity of semi-crystalline polymers.

Boron nitride nanotubes (BNNT) have high thermal conductivity as well as the property of being electrically insulating, making them of interest for applications in high power electronics. BNNT contain impurities due to the production process. They must be removed to optimize performance. A procedure of high temperature treatment in a pure oxygen environment was developed and proven to be effective at removing boron impurities from BNNT.
1. Introduction

Polyamide 11

Polyamides play a crucial role in the transport of crude oil. Due to this important task, it is important to understand the kinetics of degradation to maintain efficiency and prevent an environmental disaster. Crude oil is a combination of water, oil, organic acids, and nonsoluble acids and it is important to understand how these components affect the degradation of polyamides. The effect of hydrolytic degradation on the ductile-brittle transition of polymers is difficult to determine due to the complex relationships between molecular weight, crystalline content, and additives. Traditionally, molecular weight has been the main determinant of this transition, however, attention to the other components of the state of polyamide to form an accurate prediction of what determines the ductile-brittle transition is needed.

At the molecular level, chain entanglements are thought to be the key factor in determining the ductile-brittle behavior of a polymer. In semi-crystalline polymers, the chain entanglement in the amorphous region is the key to ductility. Fayolle et al found that in semi-crystalline polymers, random chain scission of the amorphous region results in a process called chemicrystallization [1]. During chemicrystallization, polymer chain fragments created by chain scission migrate into the crystalline phase, increasing lamella thickness and decreasing the thickness of the amorphous layer. This suggests that molecular weight alone may not be the sole determinant of the ductile-brittle transition.

For amorphous linear chain polymers, a critical entanglement molecular weight can be identified to indicate the onset of the ductile-brittle transition [2-5]. This knowledge has been applied to linear chain semi-crystalline polymers. However, attempts to predict the ductile-brittle transition of semi-crystalline polyamide-11 undergoing hydrolytic aging were imprecise [6-9]. Fayolle et al characterized a critical molar mass of 150 – 230 kg/mol for isotactic polypropylene, a range of 80 kg/mol [7]. Mazan et al attempted to predict the embrittlement of PA-11 through modeling, but their model predicted two different critical molecular weights that were both below the experimentally determined American Petroleum Institute (API) standard molecular weight of embrittlement [8-9]. Similarly, attempts to predict the ductile-brittle transition in semi-crystalline polymers undergoing oxidative aging have also been unsuccessful [10-13]. These studies demonstrate that the relationship between crystalline domains, chain entanglements, and molecular weight are complex.

Correlations between the molecular weight and mechanical properties, mainly ultimate strain, became the standard determinants of the ductile-brittle transition. The 2003 API technical report recommended a method for predicting the failure of offshore commercial PA11 P40TLO grade using molecular weight [14]. **Inherent viscosity is one method to determine the molecular weight of a polymer.** An inherent viscosity corrected for concentration of additives (CIV) of 1.05 dL/cm³ was considered the onset of possible failure, and a CIV of 1.20 dL/cm³ was considered a time when careful molecular weight monitoring was needed.

Given the importance that molecular weight degradation has on the performance properties of PA11, the effect of environment on the degradation kinetics has been extensively studied [15-21].

The crystalline content and molecular weight of semi-crystalline polymers are known to influence polymer performance properties [22]. Here we use the techniques of a previous publication which showed small organic acids found in crude oil accelerate the rate of degradation [23]. Using these condition, in this study the changes in molecular weight and
crystallinity are shown to be decoupled. The results show the molecular weight does not determine the ductile-brittle transition, rather, it is the crystallinity.

**Boron Nitride Nanotubes**

The modern world relies on electronic systems for everyday function. Electronics such as computers and cell phones have become so essential that the operation of many institutions would cease if they failed. The components within these electronics generate heat which negatively affect efficiency and lifespan. In aerospace, computers, motors, and communication devices are a small number of systems that could be affected by this issue. Failure of any of these systems would be disastrous. Therefore, effective thermal management is necessary. This proposed study will investigate polymer composites containing boron nitride nanotubes (BNNT) for use in thermal management applications in electronic systems.

A plethora of materials have been investigated for use to conduct heat generated by electronics. Finding materials with the right balance of mechanical, electrical, and thermal properties for each specific application is a major difficulty. For use in electrical systems, materials must be easily processed, electrically insulating, have a low coefficient of thermal expansion (CTE), high temperature stability, and have a high thermal conductance to even be considered. Many polymers meet most these requirements, exhibiting excellent mechanical properties, good processability, high electrical resistance, corrosion resistance, low CTE, high temperature stability and have low cost. The major downside is that polymers are not thermally conductive with values ranging from 0.1-0.5 W/mK [24]. Methods for increasing the thermal conductivity of polymers are currently being investigated due to their desirable properties. Incorporating nanofillers with high thermal conductivity into the polymer matrix is one of the most effective ways to increase the thermal conductivity.

The need for electrical insulation reduces the number of viable nanofillers. Carbon based nanofillers such as graphene and carbon nanotubes (CNT) as well as metal based fillers such as copper, gold, or silver have produced some of the best results in increasing the thermal conductivity of polymers so far. However, these nanofillers are electrically conductive and thus are unfit for applications in electrical systems. A promising nanofiller for use as thermal management in electronics that are BNNTs. BNNT has seven times the thermal conductivity of copper. Most important, BNNTs have high thermal conductivity while simultaneously being electrically insulating. At just 5.0 wt% BNNT, Yung et al. observed a threefold increase in thermal conductivity of an epoxy composite [25]. BNNTs also have better resistance to oxidation, structural stability, stronger interactions with polymer matrices and higher temperature stability than their carbon counterparts [26]. However, many issues must be overcome before widespread use of BNNT polymer composites can become a reality.

One of the biggest issues with incorporating these nanofillers into polymers is poor dispersion in most solvents. Nanofillers are commonly incorporated into solvents when being introduced to polymer composites as it allows for better dispersion throughout the final material. Recently, researchers have been able to disperse BNNTs in common solvents such as water and organic solvents such as chloroform after modification with either functional groups or polymer wrapping [27, 28]. To enhance the dispersion of BNNTs in different solvents, we will be investigating modifications to existing methods to functionalize the surface of BNNTs and to wrap the BNNTs in polymer. This will allow us to obtain the strongest possible interaction between the tubes and polymer matrix while also fully dispersing the nanofiller throughout the
composite. Specific functional groups and polymers will be tailored to each system to obtain good interaction since each polymer’s chemistry is different.

Another issue with thermally conductive polymer composites is the need for high filler loadings for significant increases in thermal conductivity. The thermal conductivity of polymer composites is almost entirely reliant on the properties of the nanofiller. The polymer matrix acts as a thermal barrier, making it crucial to create a network of fillers through the polymer to achieve high thermal conductivity [29]. This need for high filler loading leads to many negative side effects. High filler loadings can lead to poor processability, poor mechanical properties, and high cost which make polymer composites less appealing. BNNTs have shown promising results in this regard, forming a better conducting network at low filler loadings when compared to an aluminum nitride filler [25]. We will be investigating ways to significantly increase thermal conductivity at low filler loadings including purifying the BNNTs and orienting BNNTs within the polymer matrix. Common synthesis techniques of BNNTs implement high-temperature processes that lead to impurities within the final product. These impurities can limit the performance of these BNNTs and thus, need to be addressed. Modification to existing purification techniques will be explored to obtain as pure of a product as possible. In addition to purifying BNNTs, orientation of the BNNTs in the polymer matrix will be controlled. The alignment of BNNTs within the polymer matrix has been shown to increase thermal conductivity [29]. We believe that by combining these two methods, we can successfully increase the thermal conductivity by significant amounts while retaining the desirable properties of the polymer.

Polymers that will be used in this study include polyamides, polyimides, epoxies, and Ultem® polyetherimide due to their desirable properties such as high temperature stability and good processability. To measure thermal conductivity, techniques utilizing atomic force microscopy with a new probe will be used. To characterize the nanotube orientation, atomic force microscopy (AFM), scanning electron microscopy (SEM) and high powered optical microscopy will be utilized. Measurements of molecular weight, mechanical properties (tensile strength, ultimate strain, etc.), glass transition temperature and other properties will also be measured to ensure the composites are performing at optimal levels for aerospace applications.

2. Materials and Methods

Polyamide-11

Two extruded samples of commercial offshore grade polyamide-11 (PA-11), Besno P40TLO, were used in this study: P1 and P2. The monomer of PA-11, 11-aminoundecanoic acid is shown in Figure 1. A representation of the amorphous and crystalline regions in PA-11 is shown in Figure 2. P1 contains N-Butylbenzenesulfonamide (BBSA), a plasticizer, at 12% by weight. The starting mass average molecular weight (M_m) was 100 kDa, crystalline content of 31 J/g, and an ultimate strain of 500%. P2 had 12% BBSA, a starting M_m of 80 kDa, a crystalline content of 35 J/g, and an ultimate strain of 370%.

Figure 1. Structure of 11-aminoundecanoic acid:
PA-11 dogbones were immersed in deionized water and aqueous solutions of acetic and butanoic acid for aging. The mechanisms of acid and water catalyzed hydrolysis of polyamides is shown in Figures 3 and 4 respectively. Both the acetic and butanoic acid solutions were at a concentration of $6.3 \times 10^{-2}$ M. Samples were aged at 120°C for various lengths of time to accelerate the aging process. Ace high pressure rated glass tubes with Teflon plugs were used to contain the samples. Before sealing the tubes, oxygen was removed from the aging solutions by purging with argon to achieve a concentration below 50 ppm.

A TA Instruments Q20 Differential Scanning Calorimeter (DSC) was used to measure the crystalline content of the samples. A ramp rate of 3 °C/min was used to heat the samples under nitrogen from 40 to 220°C. The resulting plot of heat flow vs temperature was integrated linearly using TA Universal Analysis from 140 to 200°C to determine the enthalpy of fusion. The enthalpy of fusion is the heat required to melt the crystalline regions of PA-11. The enthalpy of fusion is represented by the area of the melting peak observed in the plot of heat flow vs temperature. Figure 5 is an example DSC result for unaged PA-11. To determine the percent crystallinity from this value, the experimental heat of fusion is divided by a theoretical heat of
fusion for a completely crystalline polymer. In the case of PA-11, a totally crystalline polymer has a heat of fusion of 189.05 J/g [30]. A sample calculation of the $\Delta S$ of the melting of the crystalline regions of PA-11 yielded a value of $1.84 \text{ J/g*K}^2$. This indicates that the entropy of the system increases. This is expected when molecules go from a highly ordered crystalline phase to a randomly oriented amorphous phase. The change of entropy relates to the elasticity of a polymer by the equation:

$$ f = \left( \frac{\partial E}{\partial l} \right)_T - T \left( \frac{\partial S}{\partial l} \right)_T $$

Here $\left( \frac{\partial E}{\partial l} \right)_T$ represents the change in internal energy with extension which has been shown to be zero, and the second term $T \left( \frac{\partial S}{\partial l} \right)_T$ represents the change in entropy, the cause of elasticity in a polymer [31].

Figure 5. A sample DSC run of PA-11, unaged.

To measure the $M_m$, in-line size exclusion chromatography (SEC) columns with a Wyatt miniDAWN multi-angle laser light scattering (MALLS) detector with a Wyatt Optilab 803 dynamic refractive index detector were used. The SEC columns fractionated the polymer molecules within the samples and the MALLS and refractive index detectors measured the molecular weight of each polymer fraction. ASTRa analysis software was used to calculate the mass average molecular weight. Hexafluoro-2-propanol (HFIP) was used as the mobile phase for
this analysis. Polymer solutions with HFIP at a concentration of 2mg/mL were used as samples for the $M_n$ measurements. Figure 6 shows an example of the molecular weight distribution obtained from MALLS for PA-11.

Figure 6. A sample MALLS molecular weight measurement of PA-11, unaged.

To measure the ultimate strain of the PA-11 dogbone samples, a MTS 810 material testing system with MTS 647 hydraulic wedge grips was used. The gauge length of the P1 dogbone samples was 12mm and the average thickness was 3.45mm. The gauge length of the P2 dogbone samples was 28mm and the average thickness was 1.6mm. Dogbone samples were loaded onto the grips at a pressure of about 300psi and a TestWare SX procedure was used to pull the samples at a rate of 6.35 mm/min. A stress strain curve was generated from this data as seen in Figure 7. The y-axis of this graph is stress, the internal forces that particles of a material exert on each other. The x-axis of this graph is percent elongation which represents strain, the amount of deformation a material undergoes when placed under stress. From this graph the ultimate strain, otherwise known as elongation at break, was used to determine whether the material was ductile or brittle.

Figure 7. A sample of mechanical results obtained by MTS of PA-11.
Boron Nitride Nanotubes

Samples of BNNT were obtained from BNNT LLC. These samples are known to contain impurities of hexagonal boron nitride (hBN), boron, and boron oxide. The structures of hBN, BNNT, and boron oxide can be found in Figure 8. BNNT LLC has different methods of BNNT production, varying the pressure at which the reaction to form these tubes occurs. Samples labeled as “P1” occur at a higher pressure than samples labeled as “P2”. Samples labeled as “Buckypaper” are BNNT processed into thin discs. These “Buckypapers” are made by making a dispersion of BNNT in isopropanol, sonicating the mixture to break up the BNNT network, and vacuum filtering these solutions onto Teflon filter paper.

Figure 8. structures of a) hBN, b) BNNT, and c) boron oxide.

<table>
<thead>
<tr>
<th>Ultimate Strain =333%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's Modulus =167 MPa</td>
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<tr>
<td>Ultimate Strength =41 MPa</td>
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<td>Tensile Strength =43 MPa</td>
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<tr>
<td>Yield Strength=9 MPa</td>
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<tr>
<td>Yield Strain=5%</td>
</tr>
<tr>
<td>Strain Rate =6.3 mm/min</td>
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</table>
A TA instruments Thermogravimetric Analyzer (TGA) was used to determine the boron content within BNNT samples. BNNT samples were dried at 100°C for one hour prior to TGA to remove any moisture from the sample. Approximately 1.5 mg of BNNT were used in each run and a ceramic pan was used each time. A ramp rate of 20°C/min was used to heat samples under oxygen to a final temperature of 550°C and held at that temperature for two hours. **Samples were run under oxygen to oxidize the boron impurities to boron oxide.**

A method for purification of the BNNT was developed utilizing the chemistry of boron and boron oxide. Samples of BNNT were first washed in DI water at 100°C to remove boron oxides. The BNNT samples were then run on the TGA under pure oxygen to oxidize the boron impurities to boron oxide. These samples were then washed again in DI water at 100°C to remove the newly formed boron oxide.

3. Results and Discussion
Polyamide-11 Ductile Brittle Transition Chemicrystallization

Low molecular weight acids significantly accelerate the hydrolysis aging of PA-11. The rate of change in $M_m$ is strongly affected by the composition of the aging environment. Table 1 shows that PA-11 samples aged in butanoic acid at 120°C degraded from a $M_m$ of 100 kDa to 36 kDa in 9 days, a rate of 7 kDa/Day. The butanoic acid aged samples did not reach an equilibrium, but managed to reach a $M_m$ of 9 kDa. Table 2 shows PA-11 samples aged in acetic acid at 120°C degraded at a rate of 3.6 kDa/Day. The acetic acid aged samples reached an equilibrium $M_m$ of 18 kDa. Conversely, Table 3 shows PA-11 samples aged in deionized water at 120°C reached an equilibrium $M_m$ of 36 kDa in 40 days, a rate of 1.6 kDa/Day.
Table 1. Butanoic Aged P2 PA-11 Data

<table>
<thead>
<tr>
<th>Day</th>
<th>Mw (kDa)</th>
<th>ΔH (J/g)</th>
<th>Crystallinity (%)</th>
<th>Ultimate Strain (%)</th>
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<td>33, 27, 26, 28</td>
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<td>9</td>
<td>65</td>
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Average and standard deviation for data points with 3 values or more: Day 7 – Mw_avg = 26 kDa, Mw Standard deviation = 2.9, ΔH_avg = 54, ΔH Standard deviation = 6.3. Day 10 - Mw_avg = 17, Mw Standard deviation = 1, ΔH_avg = 58, ΔH Standard deviation = 4.4. Day 12 - Mw_avg = 15, Mw Standard deviation = 3.5, ΔH_avg = 62, ΔH Standard deviation = 0.58.

Table 2. Acetic Aged P1 PA-11 Data

<table>
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<tr>
<th>Day</th>
<th>Mw (kDa)</th>
<th>ΔH (J/g)</th>
<th>Crystallinity (%)</th>
<th>Ultimate Strain (%)</th>
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<td>60</td>
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<td>74</td>
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Average and standard deviation for data points with 3 values or more: Day 6 - Mw_avg = 58 kDa, Mw Standard deviation = 9.2. Day 21 - Mw_avg = 22, Mw Standard deviation = 1.5, ΔH_avg = 60, ΔH Standard deviation = 2.5. Day 35, Mw_avg = 13, Mw Standard deviation = 3.5, ΔH_avg = 70, ΔH Standard deviation = 1.41.
Table 3. DI Water Aged P1 PA-11 Data

<table>
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</table>

Average and standard deviation for select data points with multiple values: Day 20 – Mw avg = 59 kDa, Mw Standard deviation = 0.7, ΔH avg = 61, ΔH Standard deviation = 2.8. Day 91 - Mw avg = 32, Mw Standard deviation = 0.7, ΔH avg = 75, ΔH Standard deviation = 2.1. Day 120 - Mw avg = 37, Mw Standard deviation = 4.4.
The ultimate strain of PA-11 did not correlate with the decrease in M_m. Figure 9 shows that PA-11 samples with the same M_m can have different ultimate strain as a result of the composition of the aging environment. PA-11 samples aged in both acetic and butanoic acid maintained ductile behavior at M_m in the range of 30 ±5 kDa. Butanoic aged samples after 4 and 5 days aging showed 395% and 367% ultimate strain at 33 kDa and 32 kDa respectively. Comparatively, water aged samples aged 50 to 240 days exhibited M_m from 29-40 kDa and ultimate strain values ranging from 75 to 148%. PA-11 samples aged in both acetic acid and butanoic acid remained ductile well into the 20 kDa range. PA-11 aged in acetic acid at 19 kDa exhibited an ultimate strain of 249% and PA-11 aged in butanoic acid 7 days had M_m from 22 to 29 kDa and ultimate strain values ranging from 304 to 359%. This shows that ductile behavior is possible at M_m far below the equilibrium molecular weight of PA-11 in DI water, and that M_m is not a suitable indicator for the ductile-brittle transition.

Figure 10 shows that ultimate strain decreases as \( \Delta H_{\text{fus}} \) increases. At 55 J/g, PA-11 enters the ductile-brittle transition. PA-11 samples with \( \Delta H_{\text{fus}} \) near this point begin to have a decrease in the ultimate strain to the 200-300% range. As the \( \Delta H_{\text{fus}} \) increases to 66 J/g, PA-11 samples begin to exhibit semi-ductile behavior. This is characterized by ultimate strain in the 100-200% range. At a \( \Delta H_{\text{fus}} \) of 70 J/g or more, the PA-11 samples are brittle, exhibiting ultimate strain values less than 100%. Figure 11 shows that \( \Delta H_{\text{fus}} \) and M_m are not correlated. Different values of \( \Delta H_{\text{fus}} \) are possible at the same M_m.
Figure 9. Ultimate strain as a function of molecular weight.

Figure 10. Ultimate strain as a function of heat of fusion.
Figure 11. Heat of fusion as a function of molecular weight.
Crystal forms describe the arrangement of polymer chains in the crystalline regions. The arrangement of the crystalline regions can have effects on both mechanical and thermal properties of a polymer. As the $\Delta H_{\text{fus}}$ of PA-11 samples increased, the crystal forms found within the polymer changed. The $\alpha$ phase of PA-11 is described as triclinic with hydrogen bonds arranged in defined sheets held together by van der Waals interactions. The $\alpha$ phase is characterized by a melting temperature of 188°C and x-ray diffractogram peaks at $2\theta = 7.5^\circ$, $2\theta = 20.0^\circ$, and $2\theta = 23.5^\circ$ [32]. The $\alpha$ phase is considered as the more thermodynamically stable form. The crystal form found in the starting material is the $\alpha'$ phase, characterized by a melting temperature of 181°C or 190°C and x-ray diffractogram peaks at $2\theta = 7.4^\circ$, $2\theta = 20.4^\circ$, $2\theta = 23.4^\circ$ [32]. The $\alpha'$ phase is extremely similar to the $\alpha$ phase, but it is described as a defective $\alpha$ phase.

As PA-11 degrades, the crystals rearrange over time into a mixture of the $\alpha$ and $\alpha'$ phases. Figures 12, 13, and 14 show the DSC thermograms of PA-11 samples aged in DI water, butanoic acid, and acetic acid respectively. PA-11 samples in each of the aging environments exhibit the same trend: the starting material contains a single peak; as degradation occurs, two peaks form, one melting at a lower temperature than the original peak and one melting at a higher temperature. These correspond to the $\alpha'$ and $\alpha$ phases respectively. Based on both the thermograms and diffractograms, there is evidence for both the $\alpha'$ and $\alpha$ phases in each aging environment. Figure 12 shows that PA-11 aged in DI water starts with a peak melting at 183°C and forms crystal phases that melt at 180°C and 190°C, both of which are indicative of the $\alpha'$ phase. Figure 13 shows that PA-11 aged in acetic acid starts with a peak melting at 182°C and forms a peak that melts at 188.5°C, indicative of the $\alpha'$ phase. Figure 14 shows that PA-11 aged in butanoic acid also starts with a melting peak at 183°C and forms a peak that melts at 185°C, most likely indicative of the $\alpha'$ phase. Figures 15 and 16 show the XRD diffractograms for P1 and P2 PA-11 samples respectively. Table 4 shows the locations of peaks in the x-ray diffractograms of PA-11 from this study. It appears that PA-11 in each aging environment contain the $\alpha$ phase as evidenced by a peak at approximately $2\theta = 20.0^\circ$. However, it is difficult to determine which crystal phase is being detected at $2\theta = 23.0^\circ$ since the literature values for $\alpha'$ and $\alpha$ are so close.
Figure 12. DSC thermograms for P1 PA-11 aged in DI water at 120°C

Figure 13. DSC thermograms for P1 PA-11 aged in acetic acid at 120°C
Figure 14. DSC thermograms for P2 PA-11 aged in butanoic acid at 120°C

Figure 15. XRD diffractograms for P1 PA-11 samples.
Figure 16. XRD diffractograms for P2 PA-11 samples.

Table 4. Peak locations from X-ray diffractograms

<table>
<thead>
<tr>
<th>Sample</th>
<th>Left Peak (2θ)</th>
<th>Right Peak (2θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2 P40 Dogbone Fresh</td>
<td>20.02</td>
<td>22.88</td>
</tr>
<tr>
<td>P1 NKT Fresh</td>
<td>20.12</td>
<td>22.3</td>
</tr>
<tr>
<td>P2 P40 Dogbone DI D74</td>
<td>19.98</td>
<td>23</td>
</tr>
<tr>
<td>P2 P40 Dogbone Butyric D26</td>
<td>20.14</td>
<td>23.36</td>
</tr>
<tr>
<td>P1 NKT Acetic D60</td>
<td>19.94</td>
<td>23.16</td>
</tr>
</tbody>
</table>
The Effect of Thermal Annealing on Heat of Fusion as a Function of Molecular Weight

To observe the relationship between thermal annealing and molecular weight, four different samples of PA-11 with differing $M_m$ were aged at 120°C in argon. Arkema PA-11 Besno P40TLO was extruded by Technip with a starting $M_m$ of 60 kDa and a starting $\Delta H$ of 31 J/g. PA-11 Besno P40TLO as manufactured by Arkema was extruded by NKT. It had a starting $M_m$ of 136 kDa, and a starting $\Delta H$ of 30.8 J/g. PA-11 P40 dogbone, water was a P1 Besno P40TLO PA-11 dogbone from the aging study in deionized water after 74 days at 120°C classified as P1 above. This aged sample had a starting $M_m$ of 57 kDa and a starting $\Delta H$ of 60 J/g. PA-11 P40 dogbone, butyric was a P2 PA-11 Besno P40TLO dogbone from the aging study in butyric acid aged 4 days at 120°C with a starting $M_m$ of 32 kDa and a starting $\Delta H$ of 59 J/g.

Figure 17 shows the change of heat of fusion over time for the PA-11 samples of varying molecular weight aged in argon at 120°C. Both PA-11 P1 NKT and P2 Coflexip samples experienced a change in $\Delta H_{\text{fus}}$ from 31 J/g to 52 J/g after 47 days aging. The P2 PA-11 dogbone sample aged in butyric acid increased from a $\Delta H_{\text{fus}}$ of 59 J/g to 67 J/g in nine days, but stayed constant after this initial increase, ending with a $\Delta H_{\text{fus}}$ of 65 J/g after 44 days. Similarly, the $\Delta H_{\text{fus}}$ of the P1 PA-11 dogbone sample aged in DI stayed constant, beginning at 82 J/g and ending with a $\Delta H_{\text{fus}}$ of 78 after 47 days. The increase in $\Delta H_{\text{fus}}$ for both the P1 NKT and P2 Coflexip samples are likely due to the presence of plasticizer in the as produced P40TLO that is absent in both aged samples. These results show that thermal annealing does not have a significant effect on the rate of change in crystallinity of PA-11. This supports the claim that increases in crystallinity and subsequent ductile-brittle transition are due to chemicrostallization that occurs during degradation.

![Figure 17. Heat of fusion as a function of time for samples of varying molecular weight.](image-url)
Boron Nitride Nanotubes

Boron is known to undergo an oxidation reaction at elevated temperatures. This reaction can be observed by TGA in pure oxygen and is characterized by a rapid increase in weight as seen in Figure 18. Because boron is one of the impurities found within BNNT, BNNT samples characterized by TGA under pure oxygen also exhibit a rapid weight gain due to the oxidation of boron at high temperature as seen in Figure 19. This oxidation reaction forms $\text{B}_2\text{O}_3$, a water-soluble compound. Using this method, the amount of boron within BNNT samples was quantified.

Table 5 shows the TGA results obtained for differing BNNT samples. The temperature at which this reaction occurred varied from 384°C to 488°C. The weight change due to boron oxidation was greater for P2 samples than P1 samples. P2 dirty and P2 pure buckypaper had increases of 0.590 mg and 0.0570 mg respectively while P1 dirty and P1 pure buckypaper had weight increases of 0.391 mg and 0.0370 mg respectively.

Table 5 shows that P2 BNNT samples contain more boron than their P1 counterparts. The percent weight increases due to oxidation were greater for P2 samples when compared to P1 samples. P2 dirty, P2 pure buckypaper, and P2 received 10/25/17 saw increases of 25%, 4%, and 56% respectively. P1 dirty and P1 pure buckypaper saw lower percent weight increases of 25% and 3% respectively.

The percent of boron within each sample was estimated based on the stoichiometry of the oxidation reaction:

$$4\text{B} + 3\text{O}_2 \rightarrow 2\text{B}_2\text{O}_3$$

P1 produced BNNT have less boron impurities present than P2 samples. Based on the oxidation increases the theoretical amount of boron present in P2 samples was greater than the amount in P1 samples. P2 dirty, P2 pure buckypaper, and P2 received 10/25/17 had 15%, 1.8%, and 25% boron respectively. P1 dirty and P1 pure buckypaper had 11% and 1.4% boron respectively.

P1 and P2 pure buckypaper samples had significantly less boron when compared to their dirty counterparts. P1 pure buckypaper had 1.4% boron while BNNT P1 dirty had 11%. P2 pure buckypaper contained 1.8% boron while BNNT P2 dirty had 15%. This demonstrates that a boron oxidation process followed by removal of $\text{B}_2\text{O}_3$ with water removes boron from the BNNT.
Figure 18. TGA result from oxidation of boron in pure oxygen
Figure 19. A sample TGA result from BNNT in oxygen.

Table 5. Results of BNNT TGA oxidation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Weight of Sample (mg)</th>
<th>Onset of Boron Oxidation (°C)</th>
<th>Weight Change due to Boron Oxidation (mg)</th>
<th>Percent of Total Weight (%)</th>
<th>Percent of Boron within BNNT (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1 Dirty</td>
<td>1.580</td>
<td>452</td>
<td>0.391</td>
<td>25</td>
<td>11</td>
</tr>
<tr>
<td>P2 Dirty</td>
<td>1.799</td>
<td>428</td>
<td>0.590</td>
<td>33</td>
<td>15</td>
</tr>
<tr>
<td>P2 Dirty as Received</td>
<td>1.910</td>
<td>488</td>
<td>1.07</td>
<td>56</td>
<td>25</td>
</tr>
<tr>
<td>10/25/17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1 Pure Buckypaper</td>
<td>1.374</td>
<td>404</td>
<td>0.0370</td>
<td>3</td>
<td>1.4</td>
</tr>
<tr>
<td>P2 Pure Buckypaper</td>
<td>1.463</td>
<td>384</td>
<td>0.0567</td>
<td>4</td>
<td>1.8</td>
</tr>
</tbody>
</table>
4. Conclusions

Polyamide-11

The ductile-brittle transition of polyamide-11 is fundamentally not determined by molecular weight. P1 and P2 PA-11 samples aged in acetic and butanoic acid respectively demonstrated ductile behavior with $M_w$ much lower than the literature value for the currently proposed critical $M_w$ characterizing the onset of the ductile brittle transition. This study shows that crystallinity is the fundamental molecular parameter and the most accurate indicator of the ductile-brittle transition for PA-11. PA-11 samples aged in each environment with differing molecular weights exhibit ductile behavior until a critical $\Delta H$ of 55 J/g, where they enter the ductile-brittle transition region. PA-11 exhibits semi-ductile behavior above 55 J/g. But by 70 J/g $\Delta H$, PA-11 exhibits brittle behavior. The size of the amorphous regions in the polymer matrix are the key to ductility as the crystalline regions are rigid. As crystallites develop, the volume of amorphous chain entanglement regions are reduced in size, this is the molecular basis for the effect of crystallinity on ultimate strain.

Thermal annealing plays a negligible role in the increase in crystallinity as shown by Figure 10. No significant increase in $\Delta H$ was observed for PA-11 samples of varying molecular weight at 120°C. This research shows that chemicrystallization is the mechanism that causes increase in crystallinity in PA-11 during degradation and thus is ultimately responsible for the loss of ductility.

There is no apparent correlation between the ductile-brittle transition and crystal phases present within the PA-11. Different percentages of the varying types of crystals exist when the material is brittle. The total crystallinity is seen to be the factor for determining ductility of PA-11.

Boron Nitride Nanotubes

This research demonstrates the purification method of heating in pure oxygen and washing with water at elevated temperature is effective for removing boron impurities found in BNNT samples. P2 BNNT samples have greater weight change due to boron oxidation than P1 samples. The boron oxidized in P2 samples is a greater percent of total weight than in P1 samples. P1 and P2 pure buckypaper BNNT samples have significantly less boron present due to boron oxidation and removal in water.
References


