**Introduction**

Several companies have been working in recent years to create biodegradable plastics using polyhydroxybutyrate (PHB). PHB is a member of the group of bioplastics called polyhydroxyalkanoates (PHAs). PHB is attractive as a commercial plastic due to its high crystallinity and melting temperature, but it is very brittle and degrades quickly around its melting temperature. Composites of PHB can be made with hydroxyapatite (HAp), a calcium-based mineral found in bones and teeth.

The purpose of this project was to examine the thermal properties of PHB and its composites with HAp nanoparticles of different shapes using both the conventional differential scanning calorimeter (DSC) and the new Flash DSC.

**Experimental Methods**

For the conventional DSC, samples of 5-10 mg were placed in aluminum pans to be tested. Pure PHB, 0.5%HAp-NS/PHB, and 0.5%HAp-NF/PHB composites were tested by various protocols, each of which consisted of an initial heating/cooling cycle to erase any thermal history and a second identical cycle to record an accurate glass transition, melting peak, and crystallization peak. The samples were tested through variable heating rates with constant cooling, variable cooling rates with constant heating, and identical heating and cooling rates. For the Flash DSC, samples of a few nanograms to a microgram were placed on a ceramic microchip. All three sample types were run on a protocol that maintained a constant cooling rate while increasing the heating rate with each cycle.

**Results and Discussion**

In variable heating experiments with PHB and its composites, an increase in heating rate showed an increase in melting temperature while the crystallization temperature remained constant. At slow heating rates, smaller crystals melt at a lower temperature. However, as the heating rate is increased, these crystals are not allowed time to melt separately from the larger crystals, so the overall melting temperature is increased. Because the protocol used included an isothermal step to hold the sample above its melting temperature, the crystallization temperature was not affected by the change in heating rate.

In variable cooling experiments, both the melting and crystallization temperatures decreased with the increase in cooling rate. Because most polymers crystallize slowly, the increase in cooling rate resulted in a lower crystallinity. At slow cooling rates small crystals form from the melt, causing the onset of crystallization, and then go back into the melt, but at higher rates these crystals do not have time to form, thus lowering the crystallization temperature. This lower crystallinity was achieved by the initial heating cycle, so the melting temperature recorded from the second cycle was also lowered because there were fewer and smaller crystals to melt. Both composites showed higher melting and crystallization temperatures than pure PHB. The NF particles showed higher temperatures than the NS particles at slower rates, but at the heating rates achieved by the Flash DSC the NS particles surpassed the NF in temperature.

This data indicates that at high heating rates the nucleating effect of the nanoparticles disappears, meaning the higher temperatures maintained by the composites must be attributed to properties of HAp itself. In all experiments the temperatures reported by the Flash DSC are significantly below those of the conventional DSC. All three sample types were run at 60 C/min heating and cooling on both DSCs, but the corresponding melting temperatures vary by as much as 40 °C. This difference may be due to the extreme sensitivity of nanocalorimetry, a difference in testing environments, or a calibration problem with the Flash DSC.

**Conclusions**

The results of this research show that, at conventional DSC heating rates, fiber-shaped hydroxyapatite nanoparticles act as a strong nucleating agent for PHB and spherical-shaped nanoparticles have a lesser effect. At higher heating rates the nucleating superiority of the HAp-NF/PHB composite seems to disappear and HAp-NS/PHB shows slightly higher temperatures, suggesting that properties of hydroxyapatite itself are responsible for the raised melting and crystallization temperatures, in addition to any nucleating effects. Because PHB is slow to crystallize, increased nucleation is favorable. Therefore further research should be performed to determine the nucleating effects of higher weight percentages of HAp and other nanoparticle fillers.

**Comparison of Melting Temperatures Between DSCs**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conv. DSC: 60 C/min</th>
<th>Flash DSC: 60 C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHB</td>
<td>169.6 °C</td>
<td>129.7 °C</td>
</tr>
<tr>
<td>0.5%HAp-NS/PHB</td>
<td>169.7 °C</td>
<td>153.4 °C</td>
</tr>
<tr>
<td>0.5%HAp-NF/PHB</td>
<td>170.2 °C</td>
<td>156.7 °C</td>
</tr>
</tbody>
</table>

**Figure 2:** There is a significant difference between the melting temperatures of each DSC. A difference of nearly 40 °C is seen for pure PHB, while the composites show a smaller difference of around 15 °C.

The discrepancies between melting and crystallization temperatures of the conventional and Flash DSCs are cause for further analysis. It may be that the slow-crystallizing PHB simply does not have time to crystallize at such high rates, but further experiments must be done with faster-crystallizing materials to determine this. If it is another error, such as calibration of the Flash DSC machinery, such experiments will also confirm this by showing similar discrepancies. After determining this, testing should be done with higher cooling rates on HAp composites of various weight percentages to further explore the effect of these fillers on the thermal properties and physical capabilities of PHB. Research should be done to find a filler and weight percentage that will best maintain the nucleating effect at the high heating and cooling rates used in manufacturing.

**Acknowledgments**

Special thanks to Dr. Meisha Shofner for her advising and support throughout my research experience. Thank you, also, to my graduate mentors Ji Hoon Lee and Stephanie Lin for their assistance in the lab and willingness to explain subjects I had not yet encountered in my studies.

**References**