

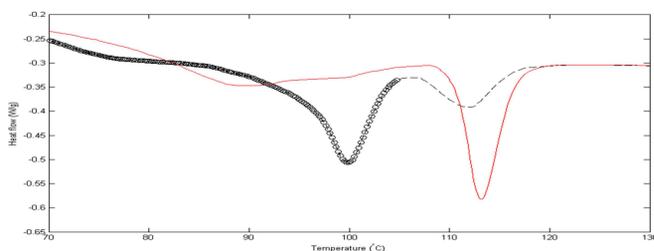
# Recycling and degradation of mechanical properties in low-crystallinity poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)

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## Introduction

Polyhydroxyalkanoates (PHAs) are a class of biopolymers capable of which can be produced through bacterial synthesis. Many PHAs have mechanical properties similar to those found in commonly used petroleum-based plastics and, as a result, have garnered interest as a potential as a more sustainable alternative to these materials. While PHAs are biodegradable, current techniques for large-scale biosynthesis require the use of large quantities of organic solvents that do not readily degrade in water and soil. As a result, the production process may incur additional environmental impacts, despite the use of more sustainable raw materials. Thus, recycling may further reduce the impact in the production and processing of PHAs.

Poly(3-hydroxybutyrate) (PHB), the most common naturally-occurring PHA, typically has a crystallinity of up to 75-85% in its homopolymer form, resulting in a brittle material that undergoes further crystallization when aged at ambient temperatures. However, a broad range of mechanical properties has been achieved with the inclusion of alternate monomer units, such as 3-hydroxyhexanoate (HHx.) Due to steric inhibition, the bulky side-chains of HHx monomers disrupt the helical crystalline structure, reducing average crystallite size and overall crystalline content. This both improves elasticity and lowers the melting point of the material but also introduces additional endothermic events between the crystallization and melting temperatures (40-160°C, Figure 1). These events have both reversing and non-reversing characteristics and have been attributed to a process of melting, crystallization, and remelting during heating. Annealing at intermediate temperatures (70-120°C) is shown to affect the relative intensity of these endothermic events. However, the effect of these treatments on material elasticity is not well-understood, which have implications on the efficacy of recycling these types of materials.

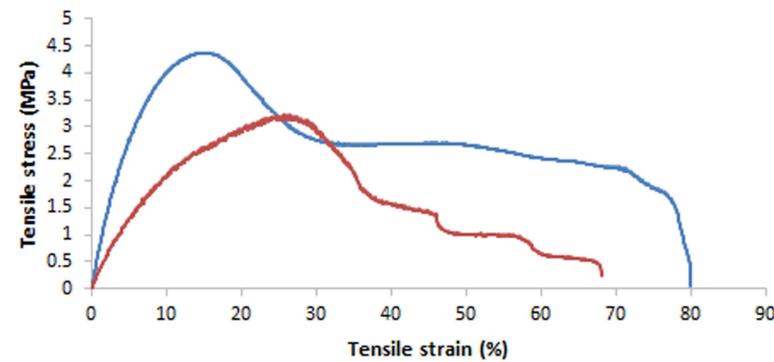


**Figure 1:** Comparison of DSC of P(HB-co-HHx) before (dotted) and after (red) annealing at 102°C for 15 minutes. A larger endothermic peak is observed at 112°C, suggesting formation of additional crystalline material during the anneal. In addition, no peak is observed between 95°C and 105°C.

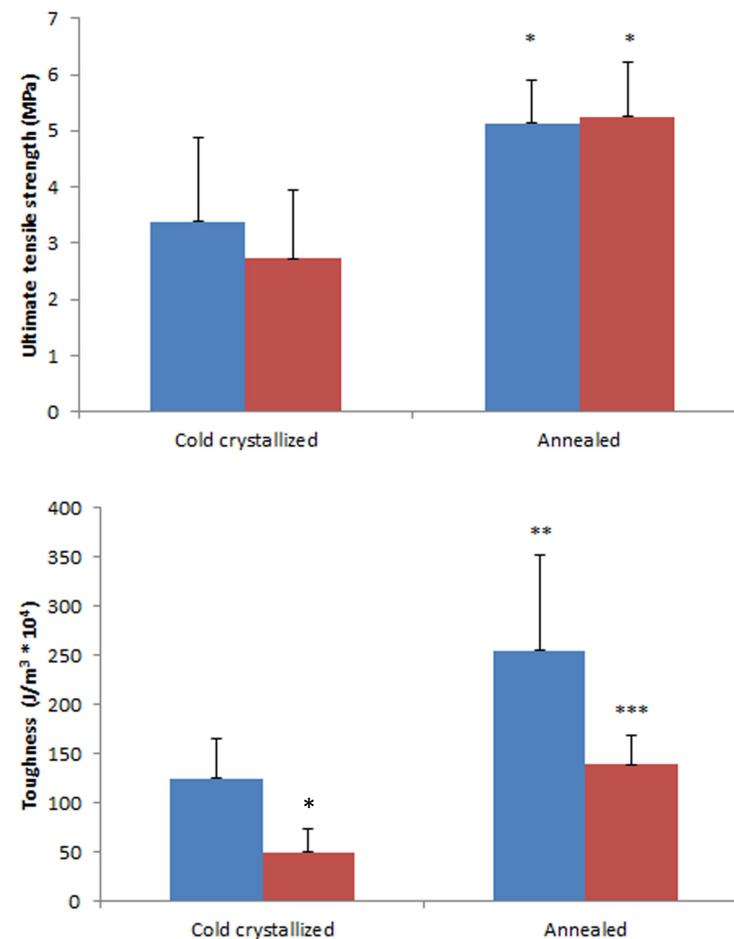
## Methods

P(HB-co-HHx) was pressed at 135°C into bubble-free sheets. After cooling to room temperature, samples were placed at 60°C for one hour for cold crystallization. Annealed samples were subject to an additional hour at 102°C before allowing to re-crystallize at 60°C for one hour. Samples were allowed to age at room temperature for 40 hours before tensile testing. Dynamic modulus was measured with dynamic mechanical spectroscopy using a single cantilever. Statistical analysis was done via Student's t test.

## Results

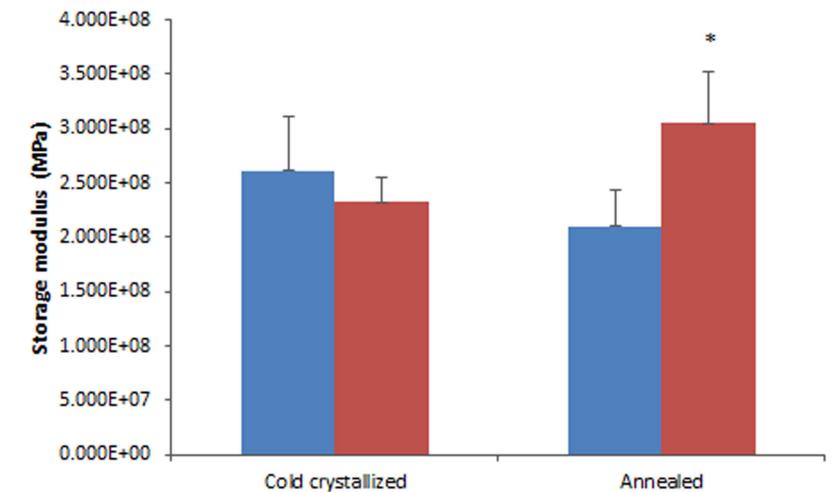


**Figure 2:** Comparison of stress/strain curves after initial casting (cycle 0, blue) and re-casting (cycle 1, red). A decrease in both ultimate tensile strength and toughness can be observed, suggesting a degradation of mechanical properties after increased exposure at 135°C.



**Figure 3:** Comparison of ultimate tensile strength (top) and toughness (bottom) for each anneal type. Loss of toughness is observed after recycling (blue = cycle 2, red = cycle 3) in both cold crystallized and annealed samples, but ultimate tensile strength does not appear to degrade. Annealed samples display both significantly higher ultimate tensile strength and toughness than cold crystallized within each processing cycle. ( $p < 0.05$ ).

## Results



**Figure 4:** Comparison of storage modulus for each anneal type. Modulus does not appear to be affected by increased exposure at 135°C (blue = cycle 2, red = cycle 3) in cold-crystallized samples. However, in annealed samples, the modulus increases. This reduction in chain mobility may be related to an overall decrease in amorphous area due to a combination of lamellar thickening during reorganization at anneal temperatures and reduced steric inhibition due to chain shortening from repeated thermal treatments

## Discussion

This study investigated the effect of two different types of repeated thermal processing on the mechanical properties of P(HB-co-HHx). When the material is repeatedly melted and isothermally crystallized at 60°C, a reduction in toughness is observed with minimal changes in ultimate tensile strength and storage modulus. However, an increase in storage modulus is observed with repeated treatments. This appears to mimic the gradual embrittlement seen in PHAs as a result of isothermal aging above  $T_g$ , which are hypothesized to be related to reduction of free amorphous volume (FAV) as inter-lamellar amorphous regions relax<sup>[1,2,3]</sup> While crystalline rearrangements due to chain shortening may contribute to the reduction of FAV, it is unlikely to be the sole mechanism, since this effect is not seen in cold-crystallized materials with similar thermal history. One hypothesis may be that the increased lamellar thickening during the anneal may further reduce the rigid amorphous fraction, which describes low-mobility amorphous chains co-localized with crystalline chains.<sup>[2]</sup> This may also explain the increased ultimate tensile strength and toughness compared to cold-crystallized material with similar thermal histories, since the relaxation of rigid amorphous regions during aging has previously been related to embrittlement of PHA copolymers.<sup>[1,2]</sup>

## References

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