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Thermo-Rheological Analysis of Polyhydroxyalkanoates (PHAs): Unravelling Thermal Degradation Mechanism for Optimal Processing

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ABSTRACT

Polyhydroxyalkanoates (PHAs), including poly(3-hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH), and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), are biodegradable thermoplastics with promising applications in sustainable materials. Understanding their thermal stability, degradation behavior, and processability is crucial for optimizing industrial applications. This study employs rheology experiments, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) to comprehensively unravel the thermal properties and degradation mechanisms of PHB, PHBH, and PHBV for optimal processing practices. Using the time-resolved method, rheological experiments were performed to assess melt stability and degradation by monitoring viscosity changes over time at elevated temperatures. As viscosity correlates with molecular weight, its decline indicates chain scission due to thermal degradation. The results show that PHB undergoes rapid viscosity loss, signaling significant degradation, whereas PHBV and PHBH exhibit enhanced thermal stability, attributed to the incorporation of HV and HH units. The obtained data provide insights into the thermal degradation mechanism of PHB, PHBV, and PHBH, showing that higher temperatures significantly accelerate thermal degradation reactions leading to viscosity loss. The onset of viscosity reduction occurs almost immediately upon exposure to elevated temperatures, particularly at higher temperatures, highlighting the sensitivity of these biopolymers to thermal processing conditions. Using the TGA under an inert atmosphere, activation energy ($E\alpha$) was calculated using isoconversional methods to understand the degradation mechanism of PHB, PHBV, and PHBH. The results confirm that PHBV and PHBH exhibit higher thermal stability than PHB, as indicated by their greater activation energies and also evidenced by the rheological measurements. DSC analysis provided additional insights into melting behavior, crystallization kinetics, and thermal transitions, showing that PHB has the highest crystallinity but is more prone to degradation, whereas PHBV and PHBH display lower degrees of crystallinity but improved thermal processability. The integration of rheology, TGA, and DSC presents a comprehensive evaluation of thermal stability, degradation kinetics, and processability of PHAs. Rheological data highlights the sensitivity of PHAs to thermal degradation, particularly at elevated temperatures, reinforcing the importance of optimizing processing conditions. These findings provide critical insights for optimizing PHAs in biodegradable polymer applications and improving their industrial processing performance.