

# Rheological Evaluation of Polyhydroxyalkanoates (PHAs) through Constitutive Equation Modelling

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## ABSTRACT

The processing of biobased, biodegradable polymers inherits rheological challenges due to the thermal instability of their molecular structure<sup>1</sup>. Polyhydroxyalkanoates (PHA) is one of these biobased, biodegradable polymers that is emerging in different applications such as food packaging. To meet the packaging needs for foods, PHAs must be designed to achieve better processability, and better performance. PHAs undergo thermal degradation as early as they start to melt. In order to understand how temperature and possible thermal degradation, influence the rheological behaviour of PHAs, Eickhoff and Harrison<sup>2</sup> investigated the dynamic rheology of PHA resins over time. The complex viscosity of the resins with two different molecular weights starts dropping after a short period of time. This viscosity reduction is more pronounced for the PHA polymers with higher molecular weights with a higher concentration of the 3-hydroxyhexanoate comonomer in their structure, indicating a greater rate of degradation. A similar observation was reported by Conrad.<sup>3</sup> They reported that higher valerate content contributes to higher viscosity values but makes the resin more susceptible to thermal degradation. To overcome these challenges, PHAs have been blended with other polymers, such as polylactic acid (PLA), to produce different products used in various applications. Bousfield<sup>4</sup> found that the composition of the PHA/PLA blend had an impact on its complex viscosity values. They showed that in comparison to 25 wt.% PLA and 75 wt.% PHA, 75 wt.% PLA and 25 wt.% PHA had higher complex viscosity.<sup>4</sup> Moreover, almost no shear thinning was observed in those compositions. Zhao *et al.*<sup>5</sup> reported that PHA/PLA blends with 90 wt.% PHA and 10 wt.% PLA exhibited much lower complex viscosity, storage modulus and loss modulus than the blend containing 70 wt.% PHA and 30 wt.% PLA at 140 °C.<sup>5</sup> Zembouai *et al.*<sup>6</sup> showed an increase in the complex viscosity of the PHA with valerate content, and PLA blend as PLA concentration increased. They demonstrated that the complex viscosity of PHA with valerate content and PLA blends follow the mixing rule with some discrepancies.<sup>6</sup> However, there is not a comprehensive study investigating the influence of the structural changes, which are inevitable during most processing, on the rheological properties and final product performance.

In this study, the rheological behaviour of PHA, in pure forms and hybrid forms with PLA, has been investigated. Dynamic, shear and extensional rheology were employed to analyze the rheological properties in a wide range of stress fields with different levels of deformation. The

generalized Maxwell model, a combination of spring and dashpot elements, was used to represent the relaxation modulus of the studied resins. Time-temperature superposition and constitutive modelling were applied to model the obtained rheological data. Also, different damping functions were used to examine the nonlinearity in viscoelastic response as a function of deformation levels. Our results showed that the rheological properties of PHA are very susceptible to temperature and residence time at high temperatures. We found that even short residence times of two minutes at the temperature of 200 °C have substantially influenced the morphology and rheological responses of PHA and PLAs containing 10 wt.% of PHA hybrid materials. The rheological data at different temperatures indicated that PHA decreases PLA/PHA's viscosity to values lower than the volumetric average values, implying PHA's contribution in changing the chain interactions within PLA morphology. However, the presence of PHA did not influence the shear-thinning behaviour of PLA. The K-BKZ constitutive equation was shown to represent the rheological properties of the resins accurately. Damping functions such as Marrucci and Wagner successfully predicted the nonlinearity of the rheological properties beyond linear viscoelastic region (LVE). Also, the extensional viscosity data revealed the reduced viscosity values for the hybrid materials to levels below the average values lower than the volumetric average values, pointing to the changes in the molecular interactions of PLA in the presence of PHA. This study reflects on the effect of processing conditions on the rheological behaviour of PHAs as biobased, biodegradable polymers and their hybrid materials in emerging markets.

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