Microstructure and rheology of polyhydroxyalkanoates: Influence of valerate content

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Introduction:

The Biodegradable poly(3-hydroxybutyrate) (PHB) and its copolymers with 3-hydroxyvalerate (HV) can be extracted from bacteria[1] or produced from the application of genetic engineering. The degradation product of PHB, the D(-)–3–hidroxybutyrate, is an intermediate metabolite naturally present in animal cells[2]. Moreover, large amounts of this product have been detected in human plasma rendering biocompatibility to PHB and leading to potential applications for therapeutic purposes[2]. The relevance of PHB and its copolymers with HV require a precise knowledge of the correlation between molecular architecture, structure and properties. The present work offers recent results in a series of PHB/HV copolymers with different HV content.

Materials and methods:

Poly(3-hydroxybutyrate) (PHB) and its copolymer of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with contents of 5 and 12 % hydroxyvalerate (HV) have been investigated by FT-IR, viscosity measurements, thermal analysis and hot stage polarized optical microscopy (POM) and rheology.

Results:

Thermogravimetric analysis indicates that the valerate induces higher thermal stability than PHB. Calorimetric studies show that the melting and crystallization temperatures shift towards lower temperatures with the addition of HV. Two melting peaks are observed in case of PHB/HV possibly due to recrystallization and melting processes taking place during the heating run[3]. A spherulitic morphology is found for all the polyhydroxyalkanoates investigated, as revealed by means of optical microscopy (Figure 1).

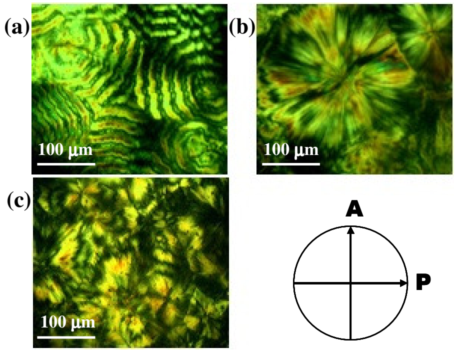

Figure 1. Morphology of (a) PHB, (b) PHB/HV 5% HV, (c) PHB/HV 12% HV.

Rheological studies show that the PHAs display a linear viscoelastic regime. The copolymer with 5% HV is predominantly elastic (G '> G") while 12% of HV becomes predominantly viscous (G' <G") (Figure 2). Moreover, steady state measurements showed that the copolymer with composition of 12% of HV satisfies the empirical rule of Cox-Merz (Figure 3).

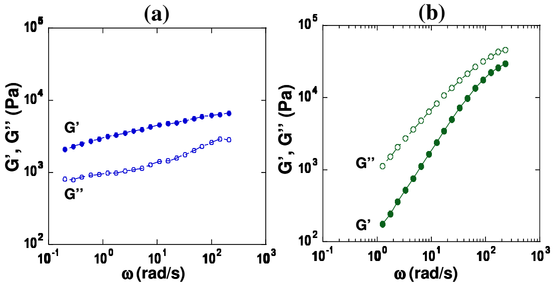

Figure 2. Viscoelastic properties of (a) PHB/HV 5% HV at 170°C; (b) PHB/HV 12% HV at 165°C.

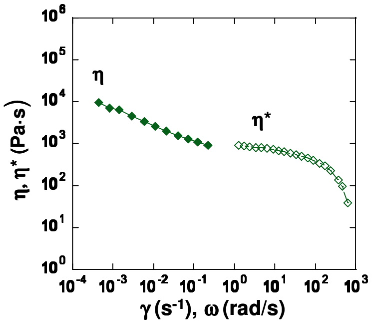

Figure 3. Steady and dynamic viscosity of PHB/HV 12% HV at 165°C.

Conclusions:

DSC showed that HV two melting endotherms, suggesting a heating-induced recrystallization. HV reduced the melting transition but increased the thermal stability, opening up the possibility of melt processing.

References:

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Abstract #845