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Novel Biodegradable Ester-Based Polymer Blends with Ethylcellulose

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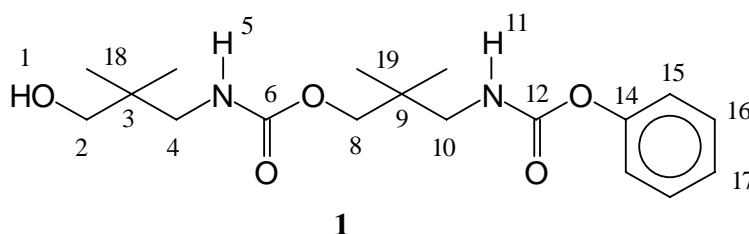
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Summary: Two PHB/EtC (poly(3-hydroxybutyrate)/ethylcellulose) blends (80/20 and 50/50 w/w) were selected for biodegradation experiments in activated sludge and in enzymatic solution of PHB-depolymerase from *Pseudomonas lemoignei* and from *Aureobacterium saperdae*. Blend morphology was quite different: blend 80/20 was composed of a matrix of impinging PHB spherulites with dispersed EtC inclusions, whereas blend 50/50 was constituted of two continuous phases with interpenetrated domains. Both blends biodegraded in activated sludge but only blend 80/20 was attacked by PHB-depolymerases from *P. lemoignei* and *A. saperdae*.

Keywords: biodegradation; blends; enzymes; poly(3-hydroxybutyrate)

Introduction

Recently poly(3-hydroxybutyrate) and related bacterial poly(hydroxyalkanoates) (PHA) have attracted much attention as biocompatible and biodegradable thermoplastic polymers.^[1-4] Degradation of PHAs occurs both in vivo through hydrolysis of the ester linkage, and in an accelerated fashion in the environment, due to the intervention of extracellular enzymes produced by microorganisms present in soil and water.



PGA is the simplest linear aliphatic polyester. The hydrophilic nature of the ester bond allows the polymer to be hydrolytically degraded by body fluids. It is a semi-crystalline thermoplastic with a

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high melting point of 224-227 °C^[2] and a glass transition temperature of around 37 °C.^[3] It has a very low solubility in most organic solvents.^[4] The unit cell contains two molecular chains in a planar zig-zag conformation within an orthorhombic unit cell.^[5]

Morphology

Microtomed sections of PHB/EtC blends (80/20 and 50/50) were observed between the crossed polars of an optical microscope (Figure 1). The micrograph of blend 80/20 (Figure 1) shows a large spherulite which nucleated on the film surface and grew across the whole film thickness (the dark area across the film represents one of the arms of the maltese cross). All over the section of blend 80/20, black spots are observed, that were attributed to phase-separated amorphous EtC. The morphology of this blend was confirmed by optical microscopy (OM) observations of isothermally crystallized samples (Table 1).

As an example, Figure 1 shows a micrograph of blend 80/20 after crystallization from the melt at 70 °C. Black (non-birefringent) EtC inclusions evenly distributed inside birefringent impinging PHB spherulites were observed. The spherulites exhibited the concentric extinction bands typical of PHB.^[5] The OM observations clearly showed that in blend 80/20 PHB and EtC constituted the continuous and dispersed phase, respectively.

Table 1. Thermal properties of PHB/EtC.

PHB/EtC	1st heating			2nd heating ^{a)}		
	T_m	ΔH_m ^{b)}	ΔH_m (PHB) ^{c)}	T_g	Δc_p ^{b)}	Δc_p ^{c)}
	°C	J/g	J/g	°C	J/(g · °C)	J/(g · °C)
100/0	174	78.0	78.0	2	0.55	0.55
80/20	174	64.2	80.3	5	0.44	0.55
60/40	174	45.4	75.7	5	0.34	0.57
50/50	173	32.6	65.2	3	0.30	0.60
40/60	174	25.8	64.5	5	0.22	0.55
30/70	173	19.4	64.7	3	0.18	0.60
20/80	173	8.8	44.0	3	0.11	0.55
0/100				140	0.26	

^{a)} After melt quenching.

^{b)} Per gram of whole sample.

^{c)} Per gram of PHB.

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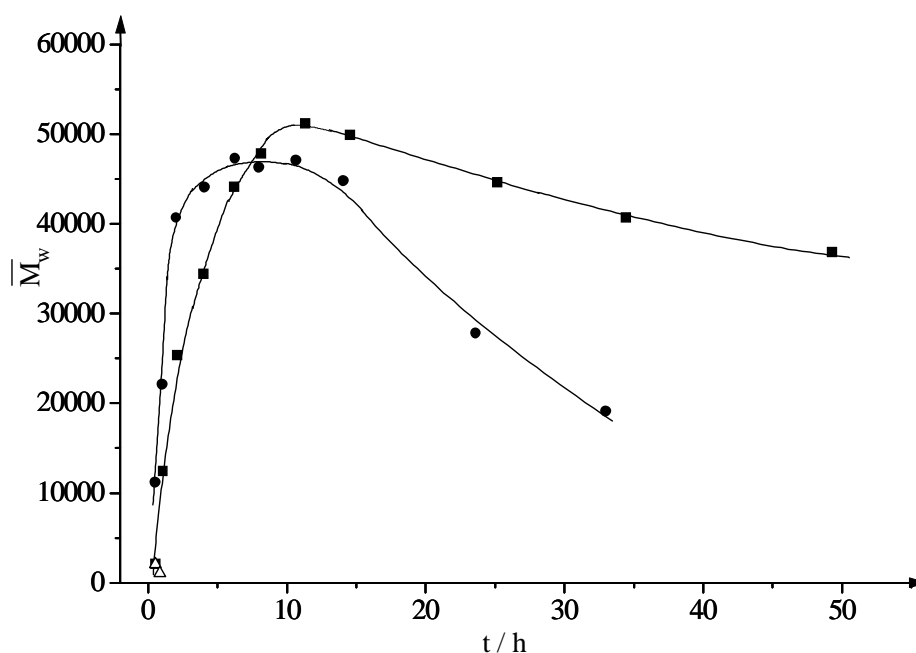


Figure 1. Weight-average molecular weight M_w of the polymer fraction as a function of time t in the polycondensation of DDPP (**3**) according to GPC in THF; reaction conditions: $T = 120\text{ }^\circ\text{C}$, $P = 1 \times 10^{-1}\text{ mbar}$, 0.84 mol-% catalyst (based on monomer units); ■ = $\text{Bu}_2\text{Sn}(\text{OOC}-(\text{CH}_2)_{10}-\text{CH}_3)_2$, ● = $\text{Bu}_2\text{Sn}(\text{OCH}_3)_2$, Δ - $\text{Ti}(\text{O}i\text{Pr})_4$.

Conclusion

It has been shown that the ring-opening polymerization of DTU is a thermodynamically disfavored process. The Gibbs energy of polymerization was found to range from 23 to 29 $\text{kJ} \cdot \text{mol}^{-1}$. However, the non substituted 6-membered cyclic urethane trimethylene urethane can be polymerized to high yields of linear polymer. The polymerization of TU is characterized by a Gibbs energy of $-18\text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K.

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