

STUDY OF THERMAL PROPERTY CHANGES OF BIOPOL/POLYAMIDE 11 BLENDS DURING BIODEGRADATION IN COMPOST

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Abstract

Polymer blends of poly(β -hydroxybutyrate-co- β -hydroxyvalerate) (Biopol) with polyamide 11, possessing copolyester continuous phase, were degraded during 25 weeks in compost. The biodegradation was followed by mass loss and melting enthalpy measurements. The degradability was primary dependent on the hydroxyvalerate content in the blend.

Keywords: biodegradability, Biopol, blend, DSC, polyamide 11

Introduction

The main advantage of the poly(β -hydroxybutyrate-co- β -hydroxyvalerate), P(HB-co-HV), well known under the trade name 'Biopol' is the stability of properties during storage and usage of molded articles and the excellent biodegradability of its wastes [1, 2]. Kumagai *et al.* [3] has found that enzymatic hydrolysis rate of poly(α -hydroxybutyric acid)(PHB) by depolymerase PHB decreases with increase of PHB crystallinity degree, whereas spherulite dimensions do not have influence on the hydrolysis rate. Tomasi *et al.* observed on the contrary at constant crystallinity degree decreasing of the enzymatic hydrolysis of PHB at increasing dimensions of the crystallinities and with increasing diameter of the spherulites.

In our paper results of investigations of crystalline structure changes caused by biodegradation of polymer blends of P(HB-co-HV) will be presented. In this case biodegradability of the P(HB-co-HV) component in the blends depends not only on its crystallinity, but also on the phase structure of the blends.

Experimental

The subject of investigation were blends of poly(β -hydroxybutyrate-co- β -hydroxyvalerate) P(HB-co-HV), with polyamide 11 (PA11). Different samples of P(HB-

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co-HV) - Biopol D300G, D400G, D600G, D610G – were submitted by Zeneca Bio Products Billingham. PA11 was an Elf Atochem commercial product.

The blends with 60% P(HB-co-HV) content were obtained with the use of laboratory double-screw extruder and the test samples were injection molded. The biodegradation was carried out in compost. Biodegradation progress was monitored by the mass loss, changes of tensile properties, melting enthalpy changes at the first heating run and by SEM examination of the surface changes.

Evaluated in this paper DSC measurements were performed using DSC7 apparatus (Perkin Elmer) under nitrogen as the purge gas. Samples of about 10 mg were placed in aluminum sealed pans. For every sample two subsequent heating runs were performed from -50 to 220°C at $20^{\circ}\text{C min}^{-1}$ heating rate.

Results and discussion

For the biodegradability investigations blends containing continuous P(HB-co-HV) phase and the highest content of polyamide 11 were chosen. These blends should undergo a degradation in compost, preferably of the copolyester phase, similarly as pure P(HB-co-HV).

From the mass loss during biodegradation in compost (Table 1) it is seen, that biodegradability increases with increasing content of β -hydroxyvalerate in the P(HB-co-HV) type used for the blends. There is also a correlation of the decreasing susceptibility to biodegradation with the increasing crystallinity degree of the P(HB-co-HV) types used in the blends with PA11.

Table 1 Mass loss of the P(HB-co-HV)/PA11 blends and of pure PA11 during biodegradation in compost

Sample	Mass loss/%			
	after 45 days	after 70 days	after 140 days	after 175 days
PA11	0.002±0.001	0.004±0.001	0.004±0.002	0.003±0.001
60% D300G/PA11	1.2±0.1	2.0±0.2	3.4±0.1	4.1±0.3
60% D400G/PA11	1.5±0.2	2.6±0.2	4.7±0.5	5.7±0.4
60% D600G/PA11	1.3±0.3	2.7±0.4	9.5±0.4	11.7±0.6
60% D610G/PA11	2.6±0.3	5.1±0.2	12.2±0.6	18.8±0.4

Melting enthalpy changes of the crystalline P(HB-co-HV) phase of the P(HB-co-HV)/PA11 blends were estimated from the first melting run. The results are collected in the Table 2 and example DSC curves for the blends with the lowest mass lost (Biopol D300G/PA11) and the highest mass loss (Biopol D610G/PA11) after biodegradation in compost are shown in Figs 1 and 2.

Melting enthalpy of the P(HB-co-HV) phase in the Biopol D300G/PA11 blend decreases by ca. 12 J g^{-1} (about 25%) after 175 days biodegradation in compost. The

same decrease in melting enthalpy of the P(HB-co-HV) phase was found in the case of Biopol D610G/PA11 blend already after 45 days of biodegradation.

Table 2 Melting enthalpy changes of the P(HB-co-HV)/PA11 blends during biodegradation in compost

Sample	Melting enthalpy of the P(HB-co-HV) crystalline phase/J g ⁻¹			
	before composting	after 45 days	after 105 days	after 175 days
60% D300G/PA11	48	40	38	36
60% D400G/PA11	30	29	27	26
60% D600G/PA11	49	46	38	36
60% D610G/PA11	34	22	18	16
PA11	47	49	47	46

Melting endotherms of the poly(β -hydroxybutyrate-co- β -hydroxyvalerate) phase in the biodegraded Biopol D300G/PA11 blends (Fig. 1), similarly to the endotherms of non-degraded samples, show two maxima, which position do not change meaningfully

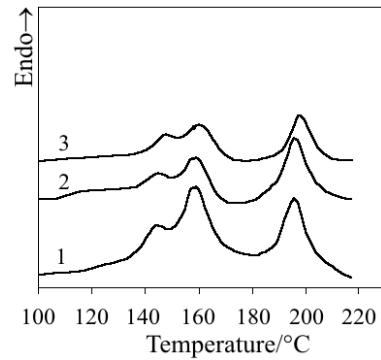


Fig. 1 DSC 1st heating runs for Biopol D300G/PA11 (60:40) blends. 1 – before composting, 2 – after 15 weeks in compost and 3 – after 25 weeks in compost

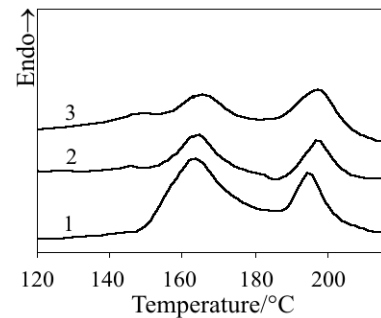


Fig. 2 DSC 1st heating runs for Biopol D610G/PA11 (60:40) blends. 1 – before composting, 2 – after 15 weeks in compost and 3 – after 25 weeks in compost

($\pm 2^\circ\text{C}$), whereas melting range of the P(HB-co-HV) phase in the biodegraded Biopol D610G/PA11 blends became broader and the appropriate endotherm shows additional maximum at lower temperatures. The width of the melting endotherm increases with the longer composting time.

Conclusions

The knowledge of structure-property relationship of environmentally compatible polymers, like poly(hydroxyalkanoate)s and their blends is especially important when considering their role at solving the issue of plastic wastes [4, 5]. Polymer blends of poly(β -hydroxybutyrate-co- β -hydroxyvalerate) with polyamide 11, like P(HB-co-HV)/PA6 blends [6, 7], are characterized by separate glass transitions for both blend's components. Generally glass transition temperature of the P(HB-co-HV) phase in the blends is slightly shifted to higher temperature and the glass transition temperature of the polyamide 11 phase is slightly shifted to the lower temperature. During composting not only biodegradation, but also complex property changes due to elevated bis 70°C temperatures are possible [8]. In case of the investigated blends the melting regions of the blends components exceeded sufficiently possible highest compost temperature. Chemical structure of the P(HB-co-HV) type in the blends influences significantly the biodegradation rate. More advanced biodegradation was observed for blend samples containing P(HB-co-HV) with higher hydroxyvalerate content of lower crystallinity degree.

Mass loss measurements of the blends and of pure polyamide 11 pointed out, that in the time scale of the experiment only the P(HB-co-HV) phase undergoes biodegradation.

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