

NOTE

Preparation of PHBV/Starch Blends by Reactive Blending and Their Characterization

M. AVELLA, M. E. ERRICO

Istituto di Ricerca e Tecnologia delle Materie Plastiche, IRTEM-CNIR, Via Toiano, 6-80072 Arco Felice (NA), Italy

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INTRODUCTION

During the last decade, the research on the biodegradable materials has received a new strong impulse by the growing interest about environmental impact of discarded plastics and resources conservation.^{1,2} Products from agricultural sources, such as starch, are considered good fillers for polymeric materials owing to their low cost, recyclability, biodegradability, and availability.³

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a family of bacterially derived polyesters.⁴ Their properties (melting temperature, glass transition temperature, crystallinity) are very similar to some widely used polyolefins (PP, PE, PET), and they can be processed using conventional extrusion and moulding process. Due to these characteristics, they are being developed and commercialized as an ideal candidate for the substitution of nonbiodegradable polymeric materials in commodities application.^{5,6} The drawbacks of PHBV are the high cost compared to that of petroleum-based commodity plastics, which prevents a larger commercial usage and a relatively low resistance to impact.⁷

A rather recent strategy to increase the biodegradability, simultaneously lowering the cost, consists of dilution of polymers with natural products.⁸ Among these latter, starch is widely available in nature, and it can be used as an additive for thermoplastic materials.⁹

In this note some results on the preparation and characterization of PHBV/Starch blends are discussed. Particularly, two methodologies of preparation were

used: a no-reactive and a reactive blending. In the first case, the composites were prepared by melt mixing the two polymers (the PHBV used has 5 mol % of HV); in the second, 2% by weight of an organic peroxide was also added.

Reactive blending is extremely popular in preparing blends in the synthetic polymer industry.¹⁰ This methodology is known to improve the compatibility and to promote the interfacial adhesion of two immiscible polymers.¹¹ The blending is performed under the conditions that promote the chemical interaction between functional groups of the two components responsible to a compatibilization of the two polymers stabilising their morphology.¹²

For both methodologies two composite compositions were prepared, having 80 and 70% in weight of the PHBV. On these blends thermal (DSC), morphological (SEM), mechanical, and biodegradation analyses were performed.

Finally, the biodegradability of the blends was also investigated, by a compost simulation test, to study the influence of starch phase on the PHBV biodegradability.

EXPERIMENTAL

Materials

Starch with high content of amylose (70%) was supplied by Cerestar. Poly-(3-hydroxybutyrate-co-valerate) (PHBV) with 5 -mol % of HV was supplied by Monsanto. Bis (*tert*-butylperoxyisopropyl)benzene, AKZO reagent-grade product, was used without further purification.

Correspondence to: M. Avella.

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Preparation of PHBV/Starch Blends

The preparation conditions used to obtain PHBV/starch blends for both methodology (a no-reactive and a reactive blending) are the following: PHBV was mixed in the melt with high-amylose starch using a Brabender-like apparatus operating at 185°C for 15 min and at 32 rpm (NR-type blends). In the case of reactive blending, 2% of the bis(*tert*-butylperoxyisopropyl)benzene was also added in the same operating conditions (R-type blends).

Impact Tests

Impact tests were performed with an instrumented Charpy pendulum (Least Autographic Pendulum MK2) at a room temperature, and at an impact speed of 1 m/s. For this test the samples (in the form of small bars with dimensions of 6.5 × 0.6 × 0.3) were notched with a fresh razor blade, ~0.2 mm depth. The final value of notch depth was measured after fracture by using an optical microscope.

The impact properties were analyzed according to the linear elastic fracture mechanism (LEFM) approach.

Morphological Analysis

Morphological analysis was carried out by using a Philips SEM 501 electron microscope. Scanning electron micrographs were taken on an Au/Pd-coated fractured surface of the dumbbell specimens.

Biodegradation Test

The biodegradability of the neat PHBV and PHBV/starch blends was investigated by a standard simulation test. This test was a modification of the ASTM D5338 procedure of controlled composting (ASTM D 5338-1992). A 3 L reactor was filled with 2 kg of mature composting material and thermostated at 55 ± 2°C. The system was continuously aerated with previously water-saturated and thermostated pressurized air. The test specimens, having the same initial shape (i.e., the same surface of exposure to the biodegradation treatment), were buried inside the reactors. The samples were withdrawn from the reactors at different times, washed with distilled water, and dried at 60°C to constant weight, and the disintegration of the materials was evaluated (referred as % of weight loss). The mature composting material was a mixture of residual sludge (municipal sewage treatment plant), grass, and wood chips (maintenance of civic parks). It was stored indoors

for several months. Prior to use, its humidity was adjusted to 60%.

RESULTS AND DISCUSSION

Blends Preparation Methodology

The PHBV/starch blends were prepared by means of two preparation methodologies a reactive (RB) and no-reactive blending (NR), according to if a little amount of an organic peroxide was added during the blending (RB). In general acceptance, the RB methodology consists of generating strong interactions (covalent bonds, ionic bonds) between two incompatible polymers to improve their interfacial adhesion, thus positively influencing the final properties of the composites.

PHBV is characterized by the presence of carboxyl groups in the backbone chains that constitute the sites of potential chemical interactions with the starch hydroxyl groups. Generally, the chemical interaction is limited to a few percent of the polymers chains, and this is sufficient to allow a good compatibilization between the two polymers. In fact, the thermal properties of the PHBV/starch blends are not dissimilar to those of PHBV, and the obtained composites can be easily processed in the same PHBV conditions.

In particular, the chemical interaction between starch and PHBV during the blending was induced by thermal decomposition of an organic peroxide. The peroxide selected was the bis(*tert*-butylperoxyisopropyl)benzene at a concentration of 2% by weight of the starch phase. Such peroxide was used owing to its $t_{1/2}$ ~30 min occurring at a temperature of 190°C. So at the temperature of blends preparation (around 185°C melting temperature of PHBV) it was possible to prevent too fast a reaction and, at the same time, keeping homogeneous blending.

As already described, the used starch is characterized by a high amylose content. It is characterized by a lower granule size and a greater number of hydroxyl groups on its surface with respect to the conventional starches. These properties allow a good dispersion of the granules in the PHBV matrix and a higher reactivity with the PHBV carboxyl groups.

Two-blend compositions were prepared having 70 and 80% by weight of PHBV for both methodologies (RB and NR).

Impact Behavior

The impact properties, obtained by Charpy-type tests, relative to neat PHBV and PHBV/starch blends (RB and NR-types) are reported in Tables I

Table I PHBV and PHBV/Starch NR Blends Impact Properties by the Charpy Method

Sample	Resilience (kJ/m ²)
PHBV	1.82
PHBV/starch 80/20 NR	1.20
PHBV/starch 70/30 NR	0.90

and II. It is evident that the impact resistance of the polymeric matrix deteriorates in the presence of starch phase as far as the NR-type composites, probably because the spherical starch granules can act as defects and stress concentrators. It can be underlined that the resilience calculated for the NR blend PHBV/starch 70/30 drops until a value of half of the neat PHBV.

On the contrary, in the case of RB-type blends (PHBV/starch 70/30), the *R*-value is comparable to that of the neat PHBV, while it is even superior when it is blended to 20% of the starch. These results can be justified by a good compatibilization reached between the two polymers by means of the action of the peroxide. Finally, it can be assessed that in the RB type the presence of also 30% of inexpensive starch blends allows keeping inalterate the impact properties of PHBV.

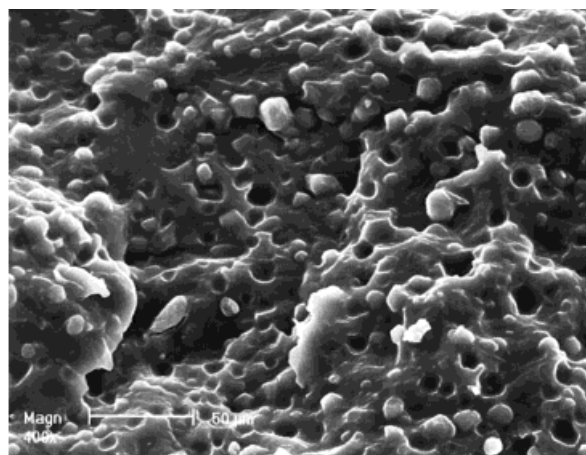
Morphological Analysis

The results on the fracture behavior can be interpreted on the basis of fractographic analysis performed by SEM on the fractured surface of notched specimens. The SEM micrographs were taken near the notch tip in the region of crack initiation.

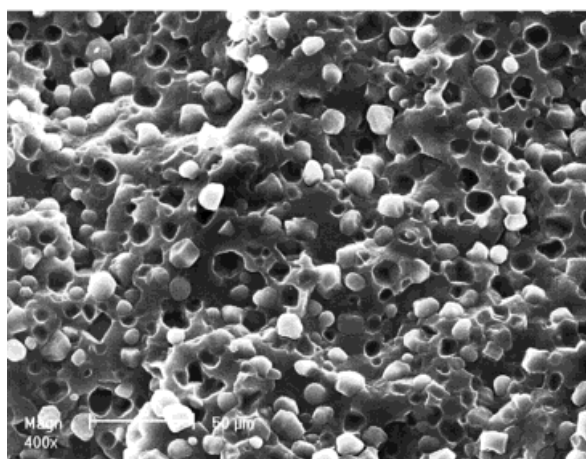
In Figures 1 and 2 the SEM micrographs related to the fractured surface of the NR and RB blends are shown, respectively. It can be outlined that the blends have a typical surface of a brittle material. In fact, they are characterised by long stepped fracture lines with no evident mechanism of crack stopping such as for the neat PHBV, (see Fig. 3). Moreover, in the case of NR-type blends, no adhesion between starch and PHBV is present. In fact, for the most part, the starch granules, after the mechanical test, pull out from the matrix; thus, the lack of adhesion between the matrix and the starch is responsible for poor impact properties of the

Table II PHBV and PHBV/Starch Blends Impact Properties by the Charpy Method

Sample	Resilience (kJ/m ²)
PHBV	1.82
PHBV/Starch 80/20 (RB)	2.10
PHBV/starch 70/30 (RB)	1.85



(a)



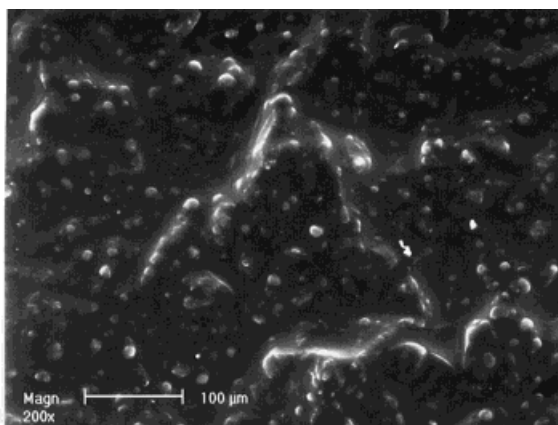
(b)

Figure 1 (a) SEM micrograph of fractured surface of PHBV/starch 80/20 blend (NR-type). (b) SEM micrograph of fractured surface of PHBV/ starch 70/30blend (NR-type).

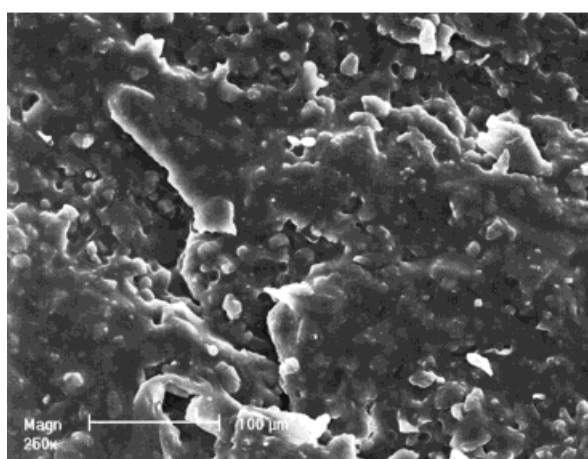
blends. On the contrary, SEM micrographs of the fractured surface of the RB-type composites show that the starch granules are well covered by the polymeric matrix, and a good interaction between the two phases is obtained. This result can be attributed to a stronger PHBV/starch interfacial adhesion generated by the presence of peroxide, giving rise to better final properties.

Biodegradation Analysis

To study the influence of the starch on the PHBV biodegradability, biodegradation tests were performed on the neat matrix, R and NR-type blends containing 30% of the starch. In Table III the results about the loss of weight of the samples (%) in a function of days of incubation are reported. As it is possible to observe, the presence of the starch is responsible for a faster biodeg-



(a)



(b)

Figure 2 (a) SEM micrograph of fractured surface of PHBV/starch 80/20 blend (RB-type). (b) SEM micrograph of fractured surface of PHBV/starch 70/30 blend (RB-type).

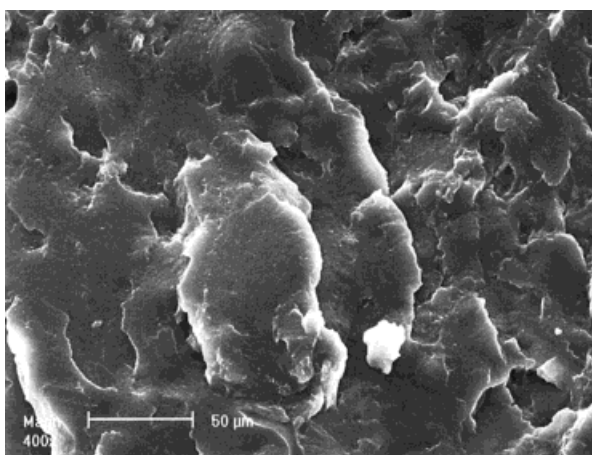


Figure 3 SEM micrograph of fractured surface of neat PHBV.

Table III Percent of Weight Loss of PHBV and PHBV/Starch Blends in the Biodegradation Test

Sample	Time of Incubation 10 days	Time of Incubation 20 days
PHBV	17%	41%
PHBV/Starch 70/30 (NR)	^a	100%
PHBV/Starch 70/30 (RB)	^a	100%

^aSamples completely pulverized so it is impossible to determine the exact weight loss.

radation than the neat PHBV. In fact, at the time of incubation of 20 days the loss of weight of the neat PHBV is 41%, while in the presence of the starch the samples are completely biodegraded. Finally, the presence of the organic peroxide has no influence on this process.

CONCLUSIONS

From this note the above-described results can be summarized.

1. Impact tests have outlined that the PHBV/starch blends prepared by means of a reactive approach (RB-type) are characterized by impact properties superior to that of the PHBV/starch NR-type blends.
2. SEM analysis performed on the fractured surface of the samples has demonstrated that PHBV/starch RB-type blends are characterized by a stronger interfacial adhesion compared to PHBV/starch NR-type blends.
3. Biodegradation tests carried out on the neat PHBV and PHBV/starch blends has revealed that the starch is responsible to a faster biodegradation than neat PHBV, and the presence of the organic peroxide has no influence on the whole process of the biodegradation of the PHBV.

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