

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Effect of Degradation on the Mechanical Properties of Multiphase Polymer Blends: PHBV/PLLA

S. Iannace^a; L. Ambrosio^a; S. J. Huang^b; L. Nicolais^a

^a Department of Materials and Production Engineering and Institute of Composite Materials

Technology, University of Naples "Federico II", Naples, Italy ^b Institute of Materials Science, University of Connecticut Storrs, Connecticut, USA

To cite this Article Iannace, S. , Ambrosio, L. , Huang, S. J. and Nicolais, L.(1995) 'Effect of Degradation on the Mechanical Properties of Multiphase Polymer Blends: PHBV/PLLA', *Journal of Macromolecular Science, Part A*, 32: 4, 881 – 888

To link to this Article: DOI: 10.1080/10601329508010301

URL: <http://dx.doi.org/10.1080/10601329508010301>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

EFFECT OF DEGRADATION ON THE MECHANICAL PROPERTIES OF MULTIPHASE POLYMER BLENDS: PHBV/PLLA

S. IANNACE* and L. AMBROSIO

Department of Materials and Production Engineering and
Institute of Composite Materials Technology
University of Naples “Federico II”
Naples, Italy

S. J. HUANG

Institute of Materials Science
University of Connecticut
Storrs, Connecticut, USA

L. NICOLAIS

Department of Materials and Production Engineering and
Institute of Composite Materials Technology
University of Naples “Federico II”
Naples, Italy

Key Words: Microbial polyester; Blend; Chemical degradation; Mechanical properties

ABSTRACT

The effect of water hydrolysis on the mechanical properties of PHBV/PLLA blends was investigated. The results were interpreted with models able to predict the Young's modulus of multiphase systems. On the basis of the experimental results relative to the pure components, the

models were used to calculate the expected values of the blends; these data were therefore compared with the experimental results in order to verify the theoretical predictions. The results show that the modulus of the degraded blends containing a low amount of PLLA is included in a range individuated from the upper and lower bound models and is close to the Halpin–Tsai prediction. This behavior is not present when PLLA is the continuous phase, and this can be due to the reduction of the degradation kinetics of the PLLA phase when PHBV is added to the polymer and forms a partially miscible system. The strength, which depends on both molecular weight and surface erosion that determine crack initiation, decreases faster than the modulus for those systems whose degradation is accompanied with remarkable surface modifications.

INTRODUCTION

Microbial polyesters such as polyhydroxybutyrate and its copolymers with hydroxyvalerate are an interesting class of degradable polymers [1] which is receiving increasing attention in the biomedical field. Because of the absence of specific enzymes, the in-vivo degradation of these materials is claimed to occur by chemical hydrolysis due to the presence of water molecules in the body fluids [1]. Some authors have reported evidence of degradation [2–10] while others have described PHBV as nondegradable [11]. Recent work [12] showed good tolerance of PHBV copolymers implanted in rats with a degradation of about 40% after 6 months; the reduction of molecular weight was faster for systems with a high content of hydroxyvalerate.

Poly-L-lactide is a component of another interesting family of degradable materials, such as the poly(α -hydroxyacid)s used for resorbable devices and implants [13–18]. Because of their good biocompatibility, they are useful as versatile materials for many temporary therapeutic applications such as osteosynthesis, bone reconstruction, drug delivery, and suture materials [13].

In previous work [19, 20] we showed that solvent-cast films of PHBV and PLLA form heterogeneous systems whose mechanical properties can be modulated through their composition. In the present paper we analyze the effect of the chemical degradation of these blends on their mechanical properties.

MATERIALS AND METHODS

Preparation of Blends and Degradation

PHBV copolymer with 20% HV, under the trade name Biopol, purchased from Malborough Biopolymers Ltd., UK, was used in this study. PLLA was supplied by Novamont S.p.A. (Novara, Italy). Thin films of PHBV/PLLA blends with weight ratios of 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100 were prepared by casting from a solution of chloroform at room temperature. The films were then kept under vacuum overnight at 50°C to allow for the evaporation of the solvent. Films were finally thermally treated for 1 hour at 100°C.

The blends were chemically degraded in phosphate buffer solution at pH 7.4 at 37°C.

Mechanical Properties

Mechanical properties of the samples were studied with an Instron 4202 on dumbbell-shaped samples according to ASTM D 638.

RESULTS AND DISCUSSION

Figures 1 and 2 reported the stress-strain curves for different degradation times for the pure components and for the blends PHBV/PLLA 80/20 and 20/80. In these figures the behavior of the pure components is reported together with that relative to the blends whose continuous phase is constituted by the same parent polymers.

From Fig. 1(a), for pure PLLA, it is possible to observe the reduction of mechanical performance as the consequence of a reduction of the maximum strength and the maximum elongation at break. PLLA shows a yield phenomenon which is followed by a further increase of stress before rupture. As the degradation phenomenon proceeds, this region is progressively reduced until it totally disappears.

This behavior can be understood by analyzing the structure of this polymer and how it changes during degradation. The crystalline regions contain highly ordered sequences of chains which are connected by amorphous zones. The latter are formed by chains that belong to more than one crystalline region and by terminal parts of the chains. Since the first stage of degradation proceeds preferentially in

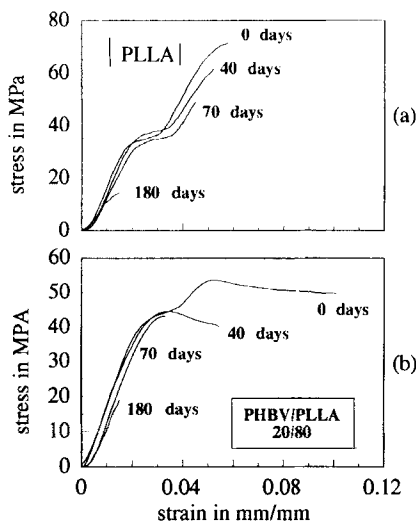


FIG. 1. Stress-strain curves at different times of degradation for PLLA (a) and the blend PHBV/PLLA 20/80 (b).

the amorphous regions, the stress which is transferred between ordered crystalline regions decreases, and this might result in a progressive reduction of Young's modulus. As a matter of fact, hydrolysis of the amorphous region is usually accompanied by an increase of crystallinity [21, 22], and for this reason the variations in Young's modulus are not easily predicted.

The gradual disappearance of the sigmoidal shape and especially of plastic flow after yield is related to degradation of the amorphous regions. The molecular chains are degraded into small fragments, and since the number of entanglements is reduced, it follows that plastic flow is also reduced. When hydrolysis of the amorphous part is complete, then plastic flow totally disappears and the curves do not present the characteristic sigmoidal shape anymore. Similar results were observed for polyglycolic acid [23].

An analogous behavior is observed for the blend containing 20% PHBV, where PLLA constitutes the continuous phase (Fig. 1b). Here the plastic flow is not characterized by a progressive increase of the stress as was observed for pure PLLA. However, chemical degradation of the amorphous phase progressively induces a reduction of plastic flow, which results in a decrease of the stress and the elongation at break. When the amorphous region is totally degraded, then no more plastic deformation is observed and the samples show brittle fracture with a low level of deformability.

Stress-strain curves of PHBV and of the PHBV/PLLA 80/20 blend were very different from the previous systems because the polyhydroxyalcanoate is above its glass transition temperature at room conditions. The stress-strain curves show a plastic flow region without any sigmoidal shape. This behavior is typical of rubbery materials; they show a high deformability which, in this case, is as high as 15%.

The degradation of the amorphous chains of pure PHBV progressively reduces the deformation of the plastic region (Fig. 2a), and the same trend is also present

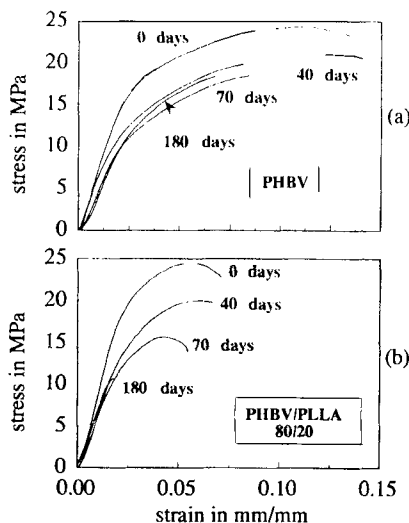


FIG. 2. Stress-strain curves at different times of degradation for PHBV (a) and the blend PHBV/PLLA 80/20 (b).

for the blend containing 20% PLLA as the dispersed phase (Fig. 2b); here the presence of the faster degradable PLLA contributes to speeding up the reduction of the mechanical performances, as we will discuss later.

The behavior of the different systems investigated are compared in Fig. 3. Here Young's modulus of the blends and the pure components are reported as relative values calculated as the ratio of the actual and the initial value of the nondegraded materials. Young's modulus of pure PLLA and the PHBV/PLLA 20/80 blend decrease very slowly at the beginning, and the decay of this mechanical characteristic becomes faster when most of the amorphous region is degraded. On the other hand, systems containing PHBV as the continuous phase show an initial decrease due to the plasticization effect followed by a constant value of the modulus versus time. From Fig. 3 it can be pointed out that the decreasing trend of Young's modulus of the blends is comparable to that of the pure components which constitute the matrix. This effect is more evident if Young's modulus of the blends is reported versus the composition of the system at each degradation time (Fig. 4). The modulus of the degraded blends is included in a range individuated by the upper and lower bound models, and they are close to those predicted by the semiempirical Halpin-Tsai equation [24].

From a practical point of view, this approach can be considered to be a good way to predict mechanical behavior during degradation of the blends at small deformation if the decreasing trend of the pure components is known. On the other hand, information given by the mechanical properties does not clearly demonstrate if there are any effects of the degradation of one phase on the mechanism of degradation of the other phase present in the blend. As a matter of fact, it is reasonable to expect that, due to the partial miscibility of the low molecular weight fractions of the polymers [20], the presence of PHBV can remove the acid fragments that result from the degradation of the PLLA chains, thus contributing to avoidance of the autocatalytic effect of the degradation of PLLA due to a local increase of pH [21, 22]. The discrepancy between the experimental data and the theoretical predictions in Fig. 4, observed for the blend containing 20% PHBV, is an indication that the degradation of the PLLA matrix is affected by the presence

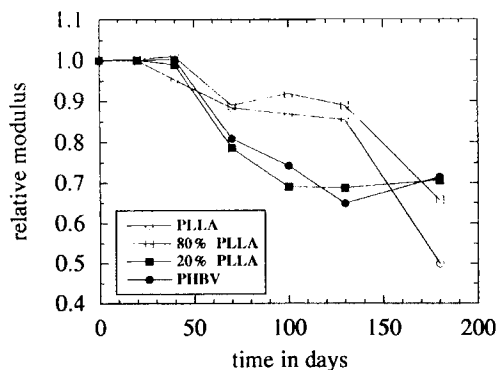


FIG. 3. Young's modulus versus time of degradation. The values are calculated as the ratio between the actual values and those relative to the systems before the degradation.

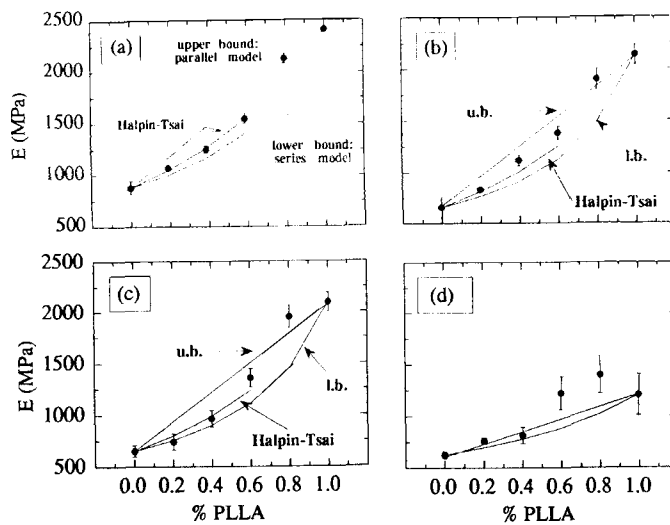


FIG. 4. Young's modulus versus the weight fraction of PLLA in the blend at different times of degradation: (a) before degradation, (b) 70 days, (c) 100 days, (d) 180 days. The experimental data are compared to the expected values calculated by the Halpin-Tsai equation, the upper and the lower bounds.

of microbial polyester in the structure. More investigations, including molecular weight measurements, are in progress with the purpose of better understanding this behavior.

The relative strength versus time for the blends is reported in Fig. 5. The decreasing trend of multicomponent materials in this case is comparable to that of the pure components which constitute the matrix of that particular blend. The lower values observed for the PHBV/PLLA 80/20 blend with respect to those of pure PHBV depend upon the surface erosion that takes place in all blends containing

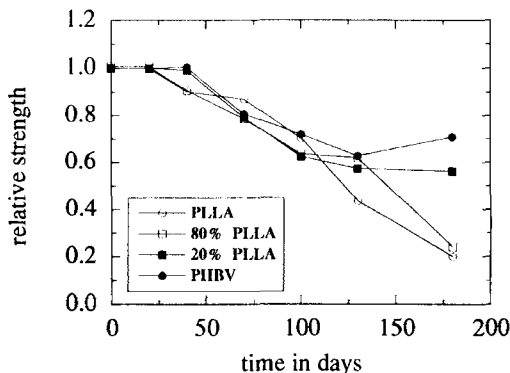


FIG. 5. Maximum stress versus time of degradation. The values are calculated as the ratio between the actual values and those relative to the systems before the degradation.

PLLA and is absent for pure PHBV. The strength, which depends on both molecular weight and surface erosion that determine crack initiation, decreases faster than the modulus. This behavior was observed for those systems whose degradation is accompanied by remarkable surface modifications.

CONCLUSIONS

The effect of degradation on the mechanical properties of a multiphase system, such as the PHBV/PLLA blend, can be interpreted on the basis of experimental results relative to the pure components. This is particularly true for properties at small deformation such as the elastic modulus. The strength, which depends on both molecular weight and surface erosion that determine crack initiation, decreases faster than the modulus for those systems whose degradation is accompanied with remarkable surface modifications.

A reasonable hypothesis is that the presence of two materials in very close domains, and the partial miscibility of low molecular weight fragments, affect the degradation of both materials: PLLA induces a faster degradation on PHBV chains and, at the same time, PHBV delays the degradation of PLLA molecules.

REFERENCES

- [1] Y. Doi, *Microbial Polyesters*, VCH Publishers, New York, 1990.
- [2] T. Saito, K. Tomita, and K. Ooba, *Biomaterials*, *12*, 309 (1991).
- [3] R. L. Kronental, in *Polymer in Medicine and Surgery* (Polymer Science and Technology, Vol. 8, R. K. Kronental, Z. Oser, and E. Martin, Eds.), Plenum Press, New York, 1973.
- [4] S. J. Holland, A. M. Jolly, M. Yasin, and B. J. Tighe, *Biomaterials*, *8*, 289 (1987).
- [5] M. Yasin, S. J. Holland, and B. J. Tighe, *Ibid.*, *11*, 451 (1990).
- [6] S. J. Holland, M. Yasin, and B. J. Tighe, *Ibid.*, *11*, 206 (1990).
- [7] J. C. Knowles and G. W. Hastings, *Ibid.*, *12*, 210 (1991).
- [8] C. Doyle, E. T. Tanner, and W. Bonfield, *Ibid.*, *12*, 841 (1991).
- [9] J. E. Kemnitzer, S. P. McCarty, and R. A. Gross, *Polym. Mater. Sci. Eng.*, *66*, 408 (1992).
- [10] H. Nishida and T. Tokiwa, *J. Appl. Polym. Sci.*, *46*, 1467 (1992).
- [11] N. D. Miller and D. F. Williams, *Biomaterials*, *8*, 129 (1987).
- [12] S. Gogolewski, M. Jovanovic, S. M. Perren, J. D. Dillon, and M. K. Hughes, *Biomed. Mater. Res.*, *27*, 1135 (1993).
- [13] M. Vert, S. M. Li, G. Spenlehauer, and P. Guerin, *Mater. Sci., Mater. Med.*, *3*, 432 (1992).
- [14] J. M. Brady, D. E. Cutright, R. A. Miller, G. C. Battistone, and E. E. Hunsuck, *J. Biomed. Mater. Res.*, *7*, 155 (1973).
- [15] T. Nakamura, S. Hitomi, S. Watanabe, Y. Shimizu, K. Jamshidi, S. H. Hyon, and Y. Ikada, *J. Biomed. Mater. Res.*, *23*, 1115 (1989).

- [16] J. M. Schakenrad, P. Nieuwenhuis, M. J. Hardonk, I. Molenaar, J. Helder, P. J. Dijkstra, and J. Feijen, *J. Biomed. Mater. Res.*, **23**, 1271 (1989).
- [17] R. R. M. Bos, F. R. Rozema, G. Boering, A. J. Nijenhuis, A. J. Pennings, A. B. Verwey, P. Nieuwenhuis, and H. W. B. Jansen, *Biomaterials*, **12**, 32 (1991).
- [18] Y. Matsusue, T. Yamamuro, M. Oka, Y. Shikinami, S. H. Hyon, and Y. Ikada, *J. Biomed. Mater. Res.*, **26**, 1553 (1992).
- [19] S. Iannace, H. D. Hwu, S. J. Huang, and L. Nicolais, *Proceeding of 4th World Biomaterial Congress*, Berlin, April 24–28, 1992.
- [20] S. Iannace, L. Ambrosio, S. J. Huang, and L. Nicolais, *J. Appl. Polym. Sci.*, Submitted.
- [21] S. M. Li, H. Garreau, and M. Vert, *J. Mater. Sci., Mater. Med.*, **1**, 123 (1990).
- [22] S. M. Li, H. Garreau, and M. Vert, *Ibid.*, **1**, 131 (1990).
- [23] C. C. Chu, *J. Appl. Polym. Sci.*, **26**, 1727 (1981).
- [24] R. A. Dickie, in *Polymer Blends*, Vol. 1 (D. R. Paul and S. Newmann, Eds.), Academic Press, New York, 1978, Ch. 8.