Drying Biodegradable Poly(hydroxybutyrate-*co*-3-hydroxyvalerate) Gels in the Elongated State To Improve Their Mechanical Properties

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ABSTRACT: Polyhydroxyalkanoates are a class of biodegradable polymers that may be used more as environmentally friendly materials if their mechanical properties can be improved. We approached this goal by modifying poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) with a well-established processing technique involving crosslinking the polymer chains and then drying a swollen gel of the network under uniaxial strain. The mechanical properties of the resulting oriented films were determined in continuous extension as a function of the degree of crosslinking and the extent of strain during the drying process. Crosslinking invariably improved the toughness. Similarly, the subsequent orientation of the process generally increased the toughness as well, but in some cases, a reduction in the extensibility offset the increase in the ultimate stress at break and yielded reduced values of the toughness. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1519–1523, 2005

Key words: biodegradable polymers; crosslinking; mechanical properties; orientation; toughness

INTRODUCTION

Biodegradable polymers have become an increasingly important potential response to waste disposal and pollution problems.[1,2] One of the goals in this area of research is to develop appropriate processing techniques for improving the overall properties of this class of materials without the loss of some of their other desirable properties, such as biocompatibility, biodegradability, and bioabsorptivity. In this study, we tried to improve the mechanical properties of films made of such polymers by crosslinking the polymer chains, swelling the network with a solvent, orienting the swollen film uniaxially, and finally removing the solvent from the stretched film by evaporation. The theoretical foundation supporting this approach to mechanical property improvements has been well developed,[3–9] and has been successfully applied to a variety of polymers,[10–20] including biodegradable polymers, such as gelatin[15,16] and starch.[19,20] The technique does involve some chemical changes to the polymer, specifically crosslinking, and sometimes also the substitutions of organic groups into chains to make the chains more soluble in convenient solvents. Materials that have been modified and have promising mechanical properties must, therefore, be re-evaluated for biodegradability, as was done, for example, for gelatins.[21,22]

The biodegradable polymer of interest in this investigation is a member of the aliphatic polyester family of polyhydroxyalkanoates (PHAs).[23–28] As many as 91 different types of monomer repeat units are known to occur in such polymers.[29] Some members of this class have been derived through the fermentation of carbohydrates and fatty acids and have melting points in the potentially useful range of 60–180°C. Fine tuning the properties of these materials involves preparing copolyesters, but they can sometimes exhibit isomorphous crystallinity with relatively little improvement in the mechanical and thermal properties. The genes for these microbial polyesters, which are energy reserves in bacterial cells, are now being transferred to plants, with the promise of an agrotechnological production method similar to that for starch. The natural copolyesters have molecular weights of approximately 500,000 g/mol or greater and can be 100% isotactic.[25,30,31]

The large-scale use of such environmentally friendly materials is becoming increasingly important (e.g., in packaging applications).[1,2,25] One recently available commercial material of this type is a hydroxybutyrate–hydroxyhexanoate copolymer[38] called Nodax (Procter and Gamble Co.; see www.nodax.

com). The copolymer of interest in this investigation consisted of 3-hydroxybutyric and 3-hydroxyvaleric acids; that is, it was a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) polymer with the repeat units —CH(CH$_3$)CH$_2$COO— and —CH(C$_2$H$_5$)CH$_2$COO—, respectively.

This study focused on the properties of this copolymer, particularly after (1) the chains were crosslinked, (2) the resulting network was swollen in a solvent, (3) the resulting gel was deformed uniaxially, and (4) the elongated gel was dried in the strained state. The mechanical properties of the resulting oriented films were determined in continuous extension as a function of the degree of crosslinking and the extent of strain during the drying process. The results were compared to establish the conditions for optimizing the properties of this important biodegradable polyester.

EXPERIMENTAL

Materials

PHBV was provided by Procter and Gamble Co. (Cincinnati, OH). Its composition was 22.3 mol % 3-hydroxyvalerate and 77.7% 3-hydroxybutyrate. It was a partially crystalline polymer with a density of 1.25 g/cm^3 and an approximate melting point of 145°C. The crosslinking agent, benzoyl peroxide, was obtained from Aldrich Chemical Co. (Milwaukee, WI).

Preparation of the crosslinked films

Attempts were initially made to form the desired crosslinked networks in the simplest possible way, that is, in the absence of a solvent. In this approach, the polymer sample and benzoyl peroxide were placed in a mold, which was then subjected to a pressure (ca. 10 psi) at 130–140°C.[31] The resulting film was brittle and nonuniform, and so it was unsuitable for the required procedures. Swelling equilibrium measurements confirmed that it was poorly crosslinked and, consequently, that solution casting was needed to form the films.

In the solution approach, the solvent had to dissolve both the copolymer and benzoyl peroxide, not interfere with the crosslinking reaction, and be easily removed by evaporation. The solubility parameter of the copolymer was 19.2 (MPa)$^{1/2}$,[32] which suggested methylene chloride (19.8), trichloroethylene (18.8), or chloroform (19.0). The low boiling point (~40°C) of methylene chloride required it to be used under refluxing conditions, and this produced a material that was insufficiently crosslinked. Similar problems were encountered with trichloroethylene, but chloroform was found to be suitable. It had a higher boiling point (~61°C) than methylene chloride and produced films

that appeared uniform and were easy to remove and dry. The amounts of the solvent had to be kept low, however, because dilution reduced the efficiency of the desired crosslinking. In a typical procedure, approximately 5 g of the polymer was dissolved in 10 mL of chloroform, and the desired amount of benzoyl peroxide was added.[31] Specifically, four series of samples were obtained with 7, 8, 9, and 10 wt % peroxide. The resulting solutions, which were clear, were then poured into Petri dishes to obtain thin uniform films. The chloroform was allowed to gradually evaporate from the solutions for 3–4 days at room temperature. The resulting films, which were white and were easily removed, were then placed in a vacuum oven at 130–140°C, and the crosslinking reaction was carried out. Higher temperatures resulted in the charring of the polymer, and this was consistent with the stability problems associated with many PHA polymers. In any case, the conditions for crosslinking this polymer were successfully established.

The films thus obtained were cut into 10 mm × 6 mm strips for the orientation procedures. The thicknesses were fixed by the diameter of the Petri dishes and the amounts of the solution, and they ranged from 0.009 to 0.012 mm.[31]

Orientation of the swollen films

For the desired orientation with uniaxial extension, the crosslinked samples were swollen to equilibrium in chloroform and then stretched with clamps alongside a ruler for the estimation of dimensional changes. The samples were then dried under tension through the evaporation of chloroform under atmospheric conditions. Because stretching reduced the thickness and breadth of the samples, films with breadths twice the lengths were swollen and stretched. The stretching ratios were either two or three times the initial lengths of the strips. The stretched films were then cut into 10 mm × 6 mm strips for the mechanical property measurements.[39]

Mechanical testing

Tests were conduced on the dried sample strips at room temperature with an Instron tester (Canton, MA), with a 2 KN cell, at a 2 mm/min rate of stretching.[31] The direction of stretching was the same as that of the extension imposed during the drying process. The results were presented as plots of the stress versus the strain. Although the focus was on the samples that had been crosslinked and oriented under strain, measurements were also carried out for uncrosslinked sample and unoriented crosslinked samples. Comparisons of these results were then used to estimate the extents of any improvements in the mechanical properties.
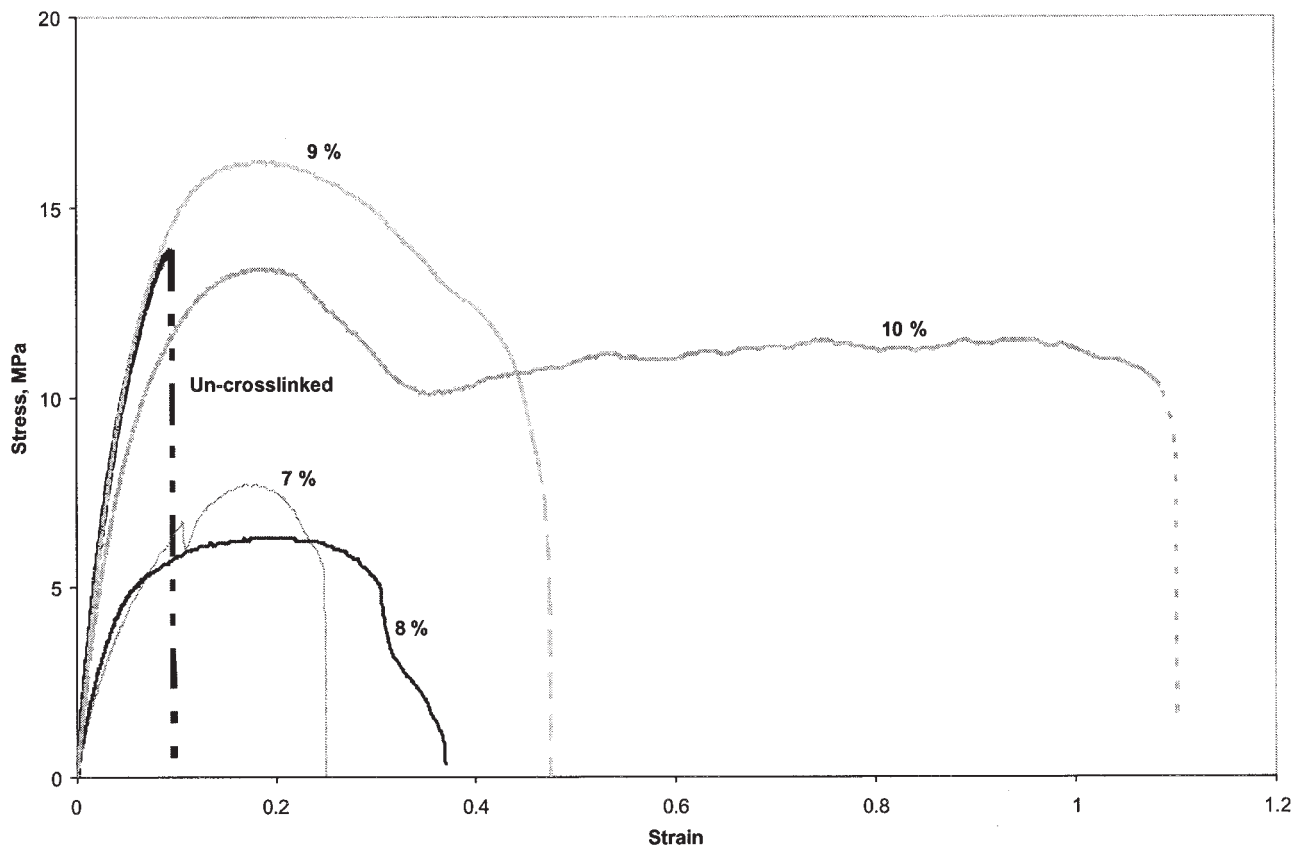
Figure 1 Dependence of the stress–strain isotherms on the degree of crosslinking for nonoriented samples not processed by drying under strain.

RESULTS AND DISCUSSION

Effects of the degree of crosslinking

Figure 1 shows the stress–strain isotherms for (1) the uncrosslinked polymer and (2) the polymer crosslinked to various extents (as described by the weight percentage of benzoyl peroxide employed) but not processed by drying under strain. Additional isotherms of this type are presented elsewhere,[31] and the complete set of values of the modulus, stress at maximum load, maximum strain (extensibility), and toughness taken from these isotherms is given in Ta-

TABLE I
Comparisons of Oriented and Nonoriented Samples

Sample	Approximate L/L_i during drying	Young's modulus (MPa)	Stress at maximum load (MPa)	Maximum strain (%)	Toughness (MPa)
Not XL	1.0	304	13.9	9.7	0.87
XL with 7% peroxide	1.0	135	7.7	25.0	1.45
	2.0	59.5	4.5	54.5	2.06
	3.0	61.3	5.2	113	3.56
XL with 8% peroxide	1.0	164	6.3	36.9	1.80
	2.0	32.9	3.8	54.3	1.52
	3.0	49.5	3.9	242	6.94
XL with 9% peroxide	1.0	261	16.2	47.5	6.21
	2.0	102	4.6	107	3.93
	3.0	137	5.6	72.3	2.70
XL with 10% peroxide	1.0	249	13.4	110	12.1
	2.0	157	6.2	59.2	2.86
	3.0	62.0	8.3	329	24.5

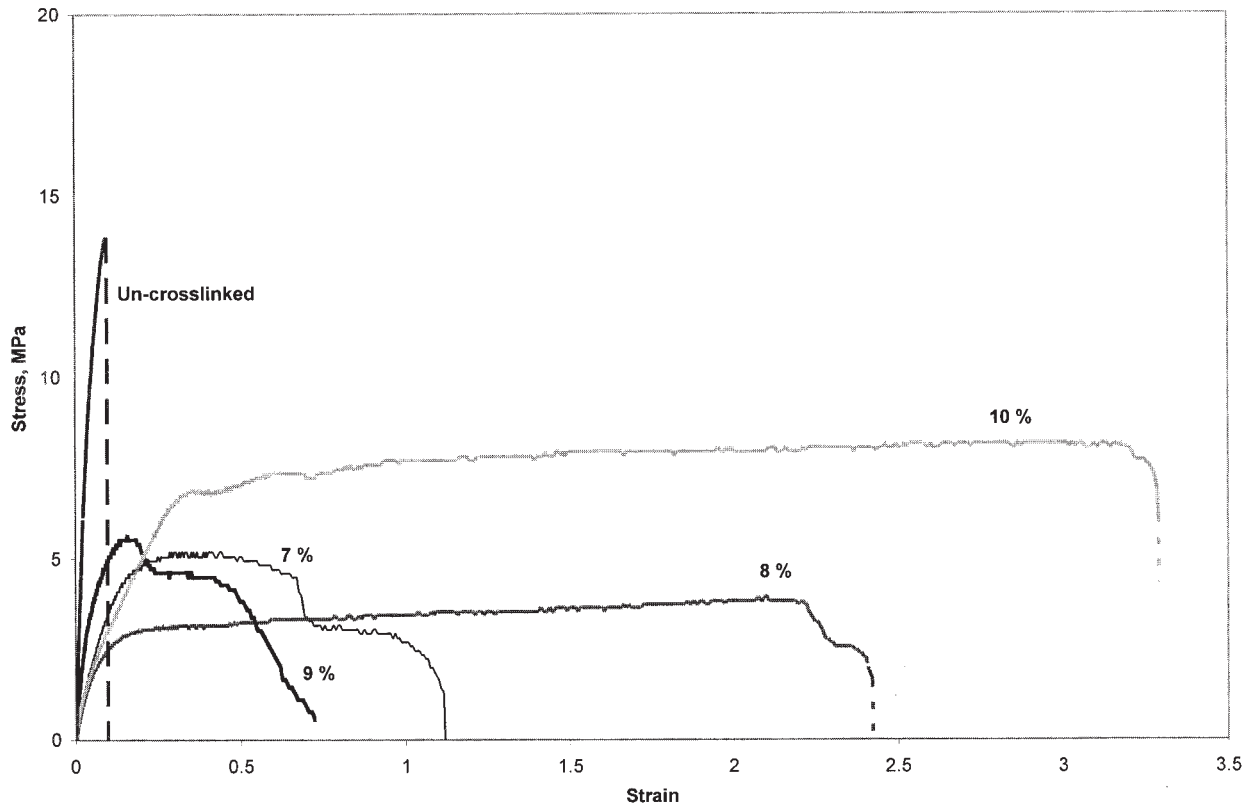XL = crosslinked; L = final length of sample after stretching; L_i = initial length of sample.

Figure 2 Effects of the degree of crosslinking for samples dried while uniaxially strained to three times their initial lengths. The weight percentage of each crosslinking agent is specified, with the reference, uncrosslinked polymer corresponding to 0%.
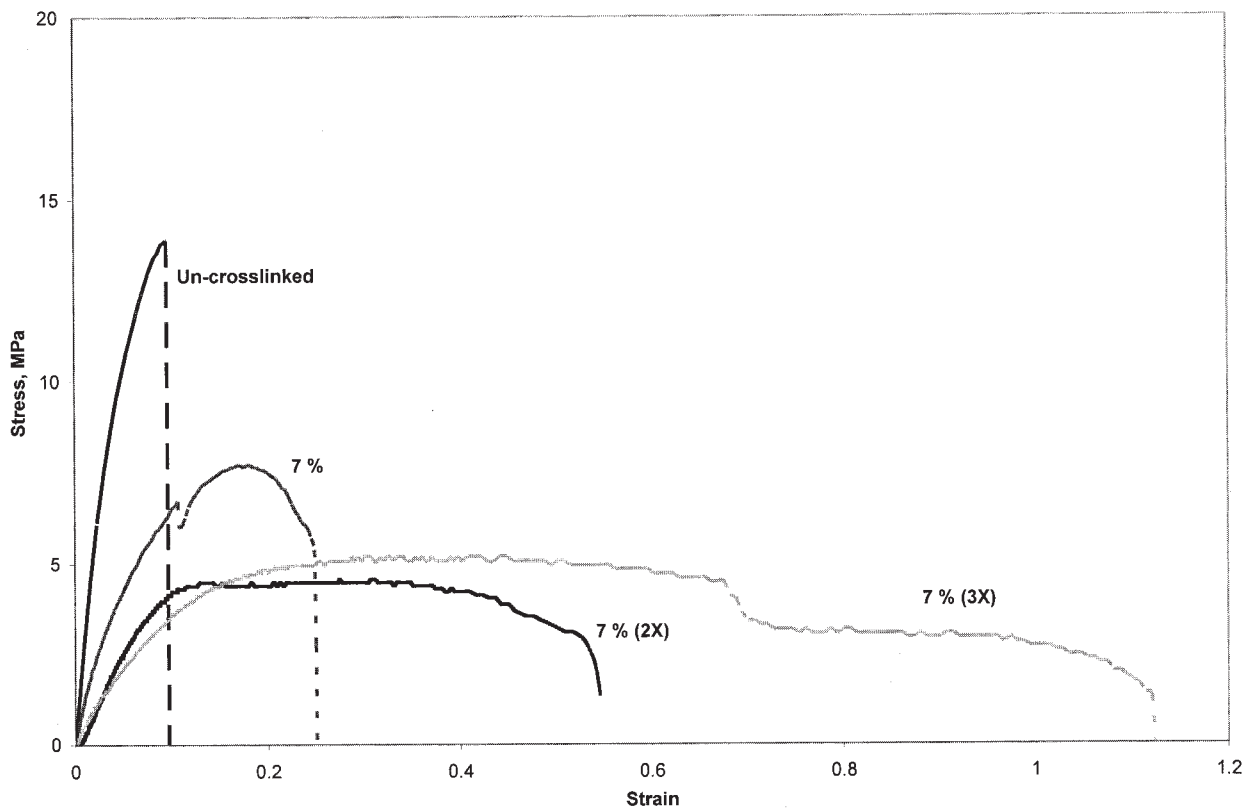

Figure 3 Effects of the degree of strain during drying for samples prepared with the 7 wt % crosslinking agent. The results for the uncrosslinked and unprocessed polymer are included for comparison.

ble I. Young's moduli of the crosslinked samples increased as the percentage of the crosslinking agent was increased, as expected. The maximum extensibilities also increased, possibly because the crosslinking reduced some of the crystallinity. Of greatest importance were the values of the toughness, as gauged by the areas under the curves. The most important point was the fact that crosslinking produced large increases in the toughness of the samples.

Effects of the degree of strain during drying

The effects of the degree of crosslinking for samples dried while uniaxially strained specifically to three times their initial lengths are shown in Figure 2. Each curve can be identified by the value specified for the weight percentage of the crosslinking agent employed, with 0% designating the reference, uncrosslinked polymer. Similarly illustrative, Figure 3 shows the effects of the degree of strain during drying for samples prepared with the 7 wt % crosslinking agent, with the results for the uncrosslinked polymer and the crosslinked but unoriented polymer included for comparison. The crosslinked samples swollen and dried under uniaxial extension frequently showed additional increases in toughness, but in some cases, reductions in the extensibility offset increases in the stress and led to decreased values of the toughness. This suggested there could be a tradeoff and indicated that there could be an optimal amount that the chains should be stretched to maximize the toughness of these materials.

CONCLUSIONS

The copolymeric polyester PHBV was put through a series of processing steps in an attempt to improve its mechanical properties. The approach involved crosslinking the chains and then drying a swollen gel of the network under uniaxial strain. The toughness of the resulting oriented films increased as the degree of crosslinking increased. An increase in the extent of strain during the drying process generally also had a beneficial effect, but in some cases reductions in the extensibility offset increases in the stress and led to decreased values of the toughness.

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