Biodegradable Natural Composites. II. Synergistic Effects of Processing Cellulose with PHB

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SYNOPSIS

This article reports on the synergistic effects observed during the processing of cellulose with bacteria-produced polyhydroxybutyrate (PHB). Cellulose fibers processed with PHB-melt exhibited defibrillation as shown by SEM. Microscopic studies of extracted fibers demonstrated that a dramatic fiber-size reduction occurred during processing. The size reduction was related to the degree of processing, which, we believe, depended on the amount of crotonic acid produced during thermal degradation of PHB. Size exclusion chromotography (SEC) studies of PHB samples thermally treated under well-defined conditions showed a decrease in molecular weight as a function of treatment time. The samples processed with and without cellulose were analyzed for their molecular weight, and the processing of cellulose was found to contribute to a greater amount of chain scission, plausibly caused by local overheating as a result of shear forces developed during processing. Thermogravimetric studies performed isothermally on PHB under various temperatures gave correlations between the amount of volatile products and the molecular weight reduction of PHB. These findings confirmed our hypothesis on *in situ* formation of acid during melt processing of PHB and hydrolysis of cellulose fibers by such an acid during compounding. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

New trends in solid waste management and rapid changes in public legislation have led scientists to increase activities on the design of materials that easily degrade under well-defined environmental conditions.[1-4] Composting is an attractive alternative for reducing solid waste and is especially suitable for waste streams consisting of food containers or hygienic articles that are impossible to reuse or recycle owing to their severe contamination. One reason why composting is not widely used is the resistance of common plastics to biodegradation. The commercial introduction of bacteria-produced polyhydroxybutyrate (PHB), a very strong candidate in the search for naturally occurring substitutes for the current high tonnage of synthetic plastics owing to its genuine biodegradability, can open new opportunities for the composting of disposable products.[5-9] Although the last 20 years of using common petrochemically derived plastics in a large variety of products has resulted in an accumulated knowledge on their properties after processing, there is only very limited experience in plastic processing of biological polymers. For example, considerations must be taken during injection-molding or extrusion to the fact that PHB and its copolymers exhibit melt instability owing to thermal degradation.[10-12] Just above the melting point, in the temperature range of 170–200°C, the principal reactions involve chain scission, which results in a rapid decrease in molecular weight. In the temperature region between 225 and 250°C, PHB is quantitatively converted, mainly to crotonic acid.[13] It has been reported that none of the conventional polyolefin stabilizers gives any significant improvement in the stability of PHB.

We have recently investigated the effects of the addition of cellulose on the properties of PHB and PHB–hydroxyvalerate (HV) copolymers. During preparation of cellulose PHB composites, it was found that the processing conditions had a great ef-

fect on the degree of dispersion of the cellulose phase in PHB.[14]

The defibrillation observed on extracted fibers suggested a possible hydrolysis of cellulose by crotonic acid formed *in situ* as a result of the thermal decomposition of the PHB. The fact that an acid can effect cellulose during processing is not new. In our laboratories, we have previously utilized the embrittlement of the cellulose phase by a hydrolytic treatment for improving the dispersion of this phase in thermoplastic composites.[15-18] The embrittlement of cellulose, brought about by the action of mineral or organic acids, is caused by a decrease in the chain length of the cellulose molecules. Prehydrolyzed cellulose was easily disintegrated in the processing equipment.[19] Another important aspect of the hydrolytic pretreatment of cellulose is the possibility for disintegrating the original cellulose fiber into fibrillar entities known as microfibrils. Among the outstanding characteristics of such fibrils are their unusually high modulus (110–137 GPa) and strength (0.8–2.0 GPa), together with high L/D ratios.[20-22]

The aim of this study has been to investigate the phenomena that take place during plastic processing of PHB in the presence of a cellulose phase. Attempts were made to optimize PHB processing conditions in order to achieve materials with improved dispersion and an interactive potential toward cellulose, which also retained good mechanical properties and an unaffected biodegradability.

EXPERIMENTAL

Materials

The matrix polymer employed was an injection-molding grade of polyhydroxybutyrate (PHB). The sample was a commercial sample (Biopol) and was kindly supplied by ICI Biological Products, Billingham, UK. The properties of the polyester used are listed in Table I. The cellulose fiber source was dissolving pulp (Ultra, Billerud, spruce, DP 764, hemicellulose content 8%, ethanol extract 0.2%, ash 0.04%).

Table I Properties of Polyesters Used

Polymer	Composition	Melt Index	Molecular Weight (M_w)
PHB	Polyhydroxybutyrate	4.0	490,000

Compounding

PHB/cellulose fiber combinations were blended for 10 min at 180°C in a Brabender kneader at 70 rpm. In other series of experiments, the processing time was varied. The compounded material was passed through a granulator, Rapid GK 20, whereafter it was subjected to a further homogenizing step in a drum mixer. A Buss-Kneader compounding extruder (Model PR 46, screw diameter 46 mm, L/D 11, exit die 6 mm) was also used for homogenization of one cellulose composite. The extruded strands were granulated before being injection-molded. All polyesters and cellulose fibers were dried at 105°C for 24 h before compounding.

Injection Molding

After homogenization, the samples were injection-molded in a conventional injection-molding machine, Arburg 221E/170 R. The molding conditions are given in Table II.

Scanning Electron Microscopy (SEM)

The tensile fracture surfaces of the composite samples were studied with a Jeol JSM-350SM scanning electron microscope operated at 10 kV. The samples were coated with 300 Å of gold.

Thermogravimetric Analysis (TGA)

The weight with respect to exposure time was determined for different temperatures using a thermogravimetric analyzer (TGA7) from Perkin-Elmer. The weight of the samples was 5–10 mg and the degradation atmosphere was static air.

Size Exclusion Chromatography (SEC)

Molecular weights and dispersities were determined by SEC using a Waters Model 510 pump, a Model 410 refractive index detector, a Waters 845 Expert Ease program for collecting data, and two mixed Styragel columns with 20 μm particles in series. Chloroform was used as the eluent at a flow rate of 1.0 mL/min. Sample concentrations of 3 g/L and injection volumes of 100 μL were used. Polystyrene standards with a low polydispersity (Polymer Lab.) were used to generate a calibration curve.

Fiber-size Determination

The length distribution was determined on both the as-received fiber material and the fibers extracted

Table II   Injection Molding Parameters

Material	Melt Temperature (°C)	Mold Temperature (°C)	Injection Pressure (MPa)	Holding Pressure (MPa)
PHB	190	45	70	58
PHB cellulose	190	45	74	67

from injection-molded composites. An optical device (Kajaani FS 100) was used to record the length of the fibers in dilute suspension while flowing through a 0.4 mm capillary. The results given below are presented as weighed length distributions.

RESULTS AND DISCUSSION

Processing of Cellulose with PHB

The cellulose fibers were processed with PHB in the way described in the Experimental section. The injection-molded samples were then placed in a Soxhlet extractor and PHB resin was removed from cellulose by dissolving in boiling chloroform. Figure 1 shows SEM photomicrographs of cellulose remaining in the extractor. The small fragments of fibers, as well as a fibrillation, show evidence of degradation occurring during the processing step. The extracted fibers were also investigated as regards their length and compared with unprocessed cellulose fibers. Figure 2 shows the cellulose fiber length distribution before and after processing with PHB. The processing of cellulose with PHB resulted in a dramatic reduction of fiber size and a very narrow fiber-size distribution. This is not a typical result of the processing of cellulose with plastics.[23] Fiber size reduction combined with extensive fibrillation, as observed by SEM, has been previously experienced when acid hydrolysis was applied.[19]

In a series of experiments, cellulose fibers were processed with PHB in a Brabender during various periods of time. Figure 3 shows the fiber length as a function of processing time. During the first 2 min, reduction of fiber size is very significant. In the following 8 min of processing, the fiber size is reduced but at a lower rate. Only after 20 min of processing does the fiber reduction level off. The degree of dispersion of the cellulose phase in the PHB matrix was gradually improved with increased processing time. Figure 4 schematically shows possible reactions that may take place during the processing of PHB with cellulose in an extruder or a Brabender.
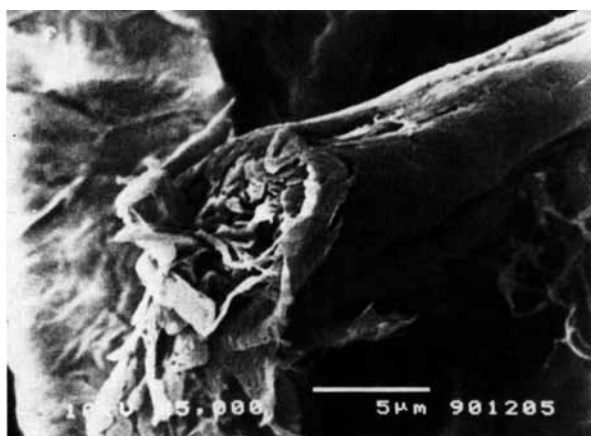
If acid could be formed during processing, this would explain the observed fiber-size reduction and the better dispersion.

Molecular Weight Reduction

We have started an investigation of the effect of temperature and time on structural changes in PHB.
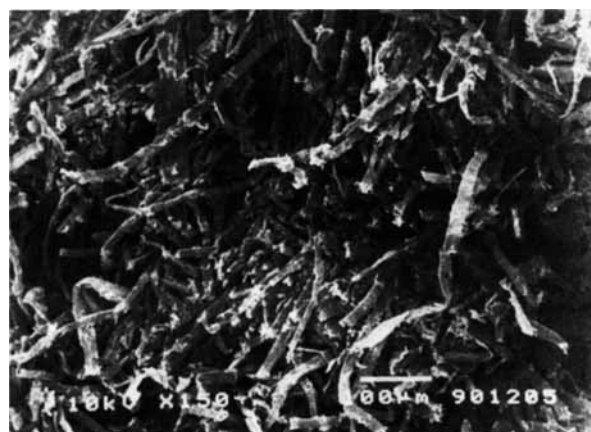
(A)

(B)

Figure 1   SEM of cellulose fibers remaining after extraction from an unloaded sample of PHB: (a) magnification ×150; (b) magnification ×5000.
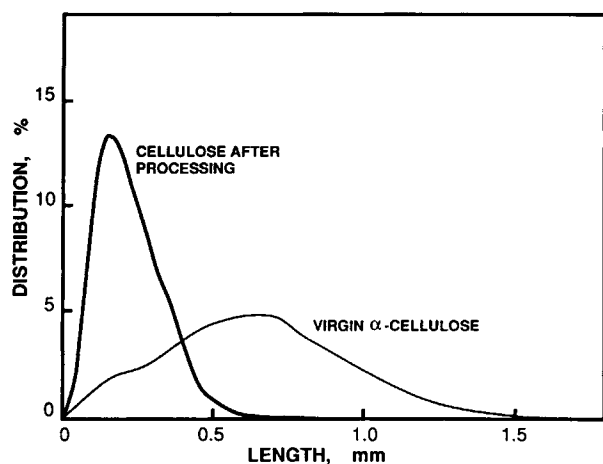
Figure 2   Fiber length distribution before and after processing with PHB.

Samples of PHB were first exposed to 200°C for various periods of time. Table III summarizes the results of determinations of molecular weight by SEC of samples exposed for 10, 20, and 30 min, and Figure 5 shows SEC chromatograms. The reduction of the weight number-average (M_n) during the first 10 min is very dramatic (greater than 10 times). The rate of molecular weight reduction decreases over the following 20 min of exposure. It can also be clearly seen from Figure 5 that the molecular weight distribution became narrower.

The reduction of molecular weight is evidence of the chain scission occurring at elevated temperatures, depending on exposure time. To obtain more information on the rate of degradation during the first few minutes, a new series of experiments was carried out with exposures of 1, 2, 3, 4, and 5 min.
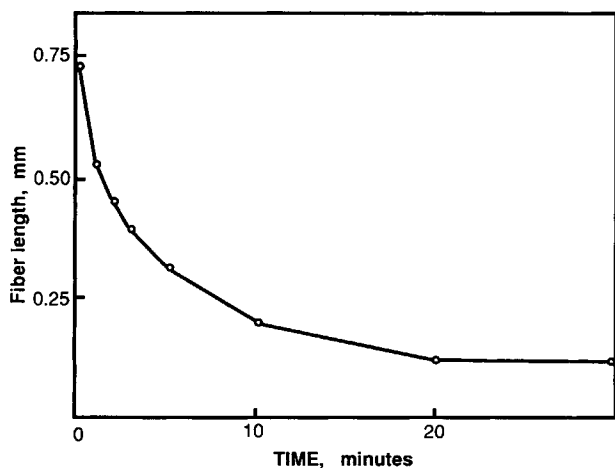

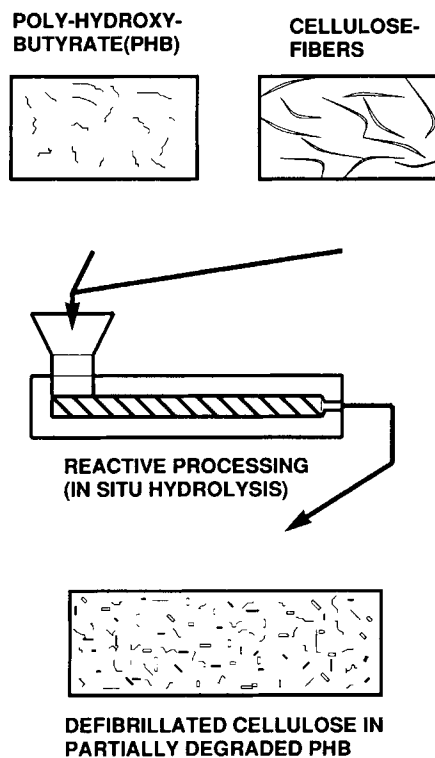**Figure 3**   The effect of processing time on fiber length.

Figure 4   Schematic illustration of reactive processing of cellulose and PHB.

Figure 6 summarizes the SEC results. Very short exposure times (1 min) actually resulted in increases in molecular weight. This is caused by esterification and has been previously observed and explained by Grassie et al.[13]

Increasing exposure time results in a drastic reduction in molecular weight within as brief a period as 2 min. Most of the molecular weight reduction occurs between 2 and 5 min. The effect of plastic processing of PHB and the introduction of cellulose on molecular weight can be studied by comparing the molecular weight of injection-molded samples with and without cellulose; the cellulose composite was obtained by compounding in the Buss extruder followed by injection-molding. SEC results of these

Table III   Polymer Degradation

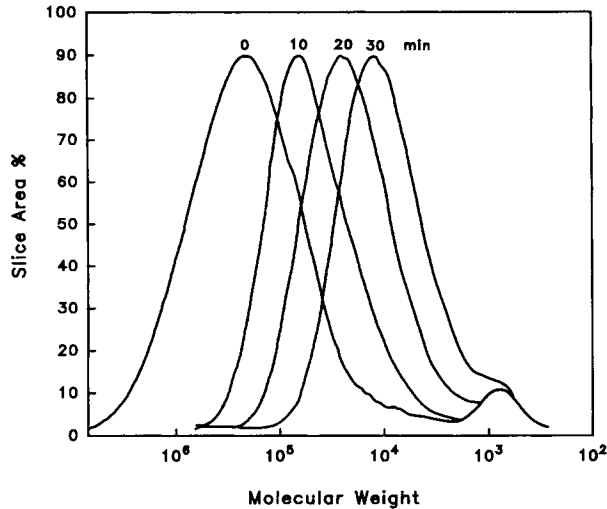| Exposure Time (Min)	M_n	M_w
0	183,000	490,000
10	12,000	72,000
20	9,000	33,000
30	5,000	16,000

Figure 5 SEC curve chromatograms of PHB exposed to 200°C for various periods of time.

samples are also included in Figure 6. There is a great difference in the molecular weight reduction between samples processed and injection-molded with and without cellulose.

It can be clearly seen that a significant degree of chain scission had already occurred during processing and injection-molding of PHB without cellulose. A further reduction in molecular weight owing to the introduction of cellulose can be explained by the fact that such processing induces high shear stresses, which, in turn, create local overheating.

Degradation Process

The schematic degradation process of PHB is shown in Figure 7. The chain scission that occurs at random, by way of an ester decomposition mechanism involving a six-membered ring transition state, continues until oligomers are formed that are volatile enough to be liberated. It has been shown that tetramers, trimers, and, especially, dimers are formed (41.2%). Crotonic acid was indicated to be the second most abundant volatile degradation product of PHB.[13] It should also be pointed out that, as a consequence of the chain scission, carboxylic acid endgroups are formed as well. The presence of such groups may improve the interactive potential when polymers are used together with other materials.

Figure 8 shows TG traces for PHB exposed to various temperatures. While the weight loss is very small at exposures to 180 and 190°C, it becomes significant at 200°C. At 210°C, the rate of degradation is much higher. To correlate the chain scission, as detected by SEC, with the formation of volatile products, as measured by TGA, a plot illustrated in Figure 9 was constructed from the data obtained at 200°C in Figures 6 and 8. Using this plot, we were able to estimate the amount of volatile products, mainly acids, that was produced during the processing of cellulose with PHB in the Buss extruder followed by injection-molding. The reduction in molecular weight (number-average, M_n) from 183,000 to 32,000 was measured on such samples. Such a reduction corresponds to the formation of
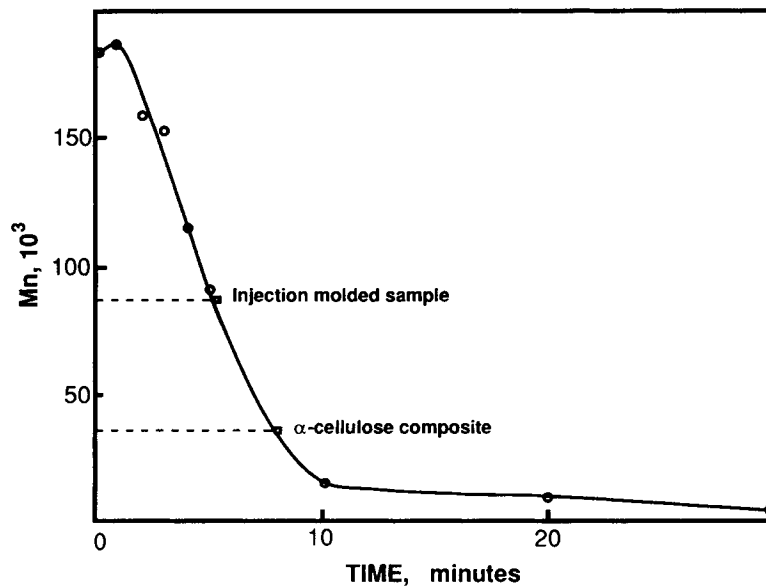

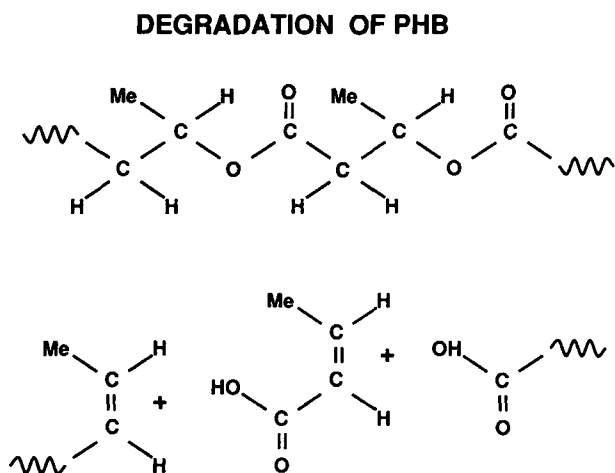**Figure 6** Molecular weight (M_n) vs. time exposure at 200°C.

DEGRADATION OF PHB

Figure 7 One of the possible paths of thermal degradation of PHB.

Figure 9 Correlation between reduction of molecular weight and weight reduction.

0.1% acid, as can be estimated from Figure 9. The addition of a small amount of organic acids, such as 0.1%, was found in our previous study to result in the hydrolysis of cellulose.

This remarkable behavior of weak organic acids such as oxalic acid at low concentrations (0.1–2%), which act as strong acids at high temperatures in the plastic melt, has been used in several practical applications for the disintegration of paper in waste plastics.[24]

CONCLUDING REMARKS

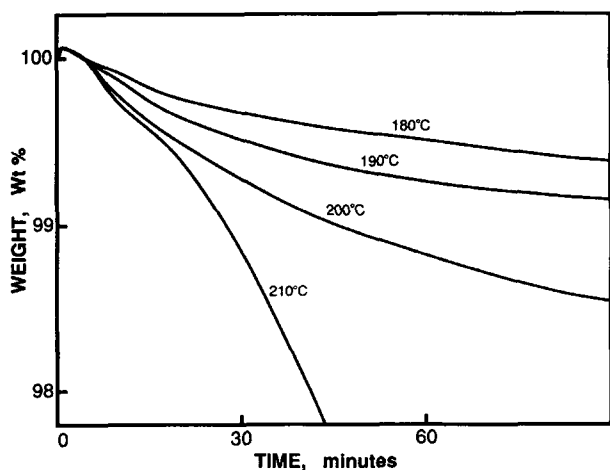We found in this study that, in plastic processing of cellulose with PHB, the cellulose fiber-size re-

duction is related to the molecular weight reduction of PHB. This means that every time chain scission of PHB occurs the fiber size is reduced. This chain scission of PHB is associated with weight reductions caused by the formation of volatile acid products, chiefly crotonic acid. This has led us to believe that acid produced during the degradation of PHB is used for *in situ* hydrolysis of the cellulose component, which yields a good dispersion of cellulose in the PHB matrix.

As the chemical reaction takes place during plastic processing of PHB at elevated temperatures, with the formation of functional groups, the occurrence of chain scission, and the formation of volatile products, the processing can be considered as reactive. When the mechanism of degradation has been clarified exactly, it will be possible to optimize the process to tailor polymers with optimal rheological and mechanical properties while still including functional groups that make possible interactions with other materials.

Figure 8 TG traces for PHB exposed to various temperatures in a static air atmosphere.

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