

Biodegradable Natural Composites.

I. Processing and Properties

P. GATENHOLM,^{1*} J. KUBÁT,² and A. MATHIASSEN²

¹Department of Polymer Technology and ²Department of Polymeric Materials, Chalmers University of Technology, S-412 96 Göteborg, Sweden

SYNOPSIS

This paper presents an investigation of the properties of composites of bacteria-produced polyesters reinforced with wood cellulose. Although cellulose fibers improved the strength and stiffness of the polyhydroxybutyrate (PHB), the samples were very brittle. The impact strength and elongation at break of these composites were significantly improved when PHB copolymers with increased amounts of hydroxyvalerate (HV) were used as the matrix. Dynamic mechanical properties of PHB copolymers of varying compositions and of cellulose-filled composites were investigated. The introduction of cellulose resulted in a decreased loss factor owing to restrictions of the chain mobility in the amorphous phase. An improvement was observed in the dynamic modulus, which was seen to be greatest at elevated temperatures. An excellent dispersibility of cellulose fibers was achieved in the PHB matrix as compared with such synthetic matrices as polystyrene or polypropylene. The degree of dispersibility was strongly affected by processing conditions. The defibrillation observed on extracted fibers suggests a possible hydrolysis of cellulose by crotonic acid formed *in situ* as a result of the thermal decomposition of the PHB matrix.

INTRODUCTION

Novel polymers are being introduced, with the aim of fulfilling new environmental requirements regarding the effective management of postconsumer waste. Bacteria-produced polyhydroxybutyrate (PHB) and PHB hydroxyvalerate (HV) copolymers, for example, are genuinely biodegradable materials in that their rate of chemical hydrolysis is very slow, but microorganisms added to such materials rapidly degrade the biopolymers to carbon dioxide and water.¹⁻³ These biopolymers exhibit mechanical properties that equal or even exceed those of traditional thermoplastics.²⁻⁵ However, the current price of such materials limits their use to a few exclusive applications such as in the field of biomedicine and chiral synthesis.^{2,6}

The incorporation of a filler contributes often to a more competitive price for thermoplastics and a general improvement in their load-bearing capability

and thermal properties. Reports have been published on the use of inorganic particulate fillers, such as calcium carbonate, china clay, and chopped glass fibers, as reinforcement for PHB and its copolymers.² Yet these composites are not biodegradable, and thus the advantage of using biodegradable matrix is lost. In this respect, a natural fiber such as wood cellulose, which is biodegradable, would be a much better choice as a filler for PHB and its copolymers. Up to this time, several reports have documented the use of wood fibers as a filler and reinforcement in such thermoplastics as polyethylene (PE), polystyrene (PS), polyvinyl chloride (PVC), and polypropylene (PP).⁷⁻¹³ However, the incorporation of a biodegradable filler, such as cellulose in a biodegradable matrix, has not been studied to a great extent.

The incorporation of cellulose fibers in a synthetic polymer is often associated with agglomeration as a result of insufficient dispersion, which obviously contributes to inferior mechanical properties. This apparent lack of compatibility between the cellulose phase and thermoplastic matrices has to do with differences in the polarity of the cellulose and hy-

* To whom correspondence should be addressed.

Table I Properties of Polyesters Used

Polymer	Composition	Melt Index	Molecular Weight
PHB	Polyhydroxybutyrate	4.0	539,000
PHB/6% HV	Polyhydroxybutyrate/ 6% polyhydroxyvalerate	3.3	810,000
PHB/10% HV	Polyhydroxybutyrate/ 10% polyhydroxyvalerate	3.8	477,000
PHB/15% HV	Polyhydroxybutyrate/ 15% polyhydroxyvalerate	10.0	646,000

drophobic matrix polymers, and several attempts have been made to overcome the problem. Graft polymers of the matrix material and a polar group have been used successfully to improve the mechanical properties of cellulose-polymer composites.^{14,15} Another approach, using hydrolysis of the cellulose fibers prior to compounding, resulted in a significant improvement in ductility and dispersibility.^{16,17}

The present paper reports on the effect of the incorporation of cellulose fibers on the mechanical properties of bacteria-produced polyesters with varying compositions. The effect of processing on the properties of cellulose-polyester composites is also investigated. Interfacial properties, including dispersibility, are examined and discussed in terms of the compatibility of various phases.

EXPERIMENTAL

Materials

The matrix polymers employed were injection-molding grade of polyhydroxybutyrate (PHB) and PHB copolymers containing various amounts of po-

lyhydroxyvalerate (HV). All samples were commercial samples (Biopol) and were kindly supplied by ICI Biological Products, Billingham, UK. The properties of the polyesters used are listed in Table I.

Polypropylene, density 905 kg/m³, melt index MI_{230/16} 13, broad MW distribution with M_n 6500, and M_w 83,600, as determined by GPC, was also used. The cellulose fiber source was dissolving pulp (Ultra, Billerud, spruce, DP 764, R18 94.2%, R10 89.8%, ethanol extract 0.2%, ash 0.04%).

Compounding

All polymer/cellulose fiber combinations were blended for 10 min at melt temperatures (see Table II) in a Brabender Kneader at 70 rpm. Two other methods were also used to mix cellulose fibers with polyesters. The selected polymer/cellulose combinations were compounded in a Buss-Kneader compounding extruder (Model PR 46, screw diameter 46 mm, L/D 11, exit die 6 mm) at 190°C. The residence time in the extruder was about 3 min. The compounded material was passed through a granulator, Rapid GK 20, whereafter it was subjected to

Table II Injection-Molding Parameters

Material	Melt Temperature (°C)	Mold Temperature (°C)	Injection Pressure (MPa)	Holding Pressure (MPa)
PHB	180	45	70	58
PHB/6% HV	170	45	72	65
PHB/10% HV	160	45	74	70
PHB/15% HV	150	45	79	67
PHB cellulose	190	45	74	67
PHB/6% HV cellulose	176	45	79	58
PHB/10% HV cellulose	176	45	88	70
PHB/15% HV cellulose	170	45	104	81

Table III The Effect of Cellulose on Tensile Modulus of Composites

Composition	Matrix	Tensile Modulus (GPa)
PS	Polystyrene	3.3
PS 20% cellulose	Polystyrene	4.8
PS 40% cellulose	Polystyrene	6.3
PP	Polypropylene	1.3
PP 20% cellulose	Polypropylene	2.5
PP 40% cellulose	Polypropylene	3.7
PHB	Polyhydroxybutyrate	3.2
PHB 20% cellulose	Polyhydroxybutyrate	2.5
PHB 40% cellulose	Polyhydroxybutyrate	6.2

a further homogenizing step in a drum mixer. A twin-screw extruder (Werner & Pfeiderer ZSK 30) was also used at 190°C for homogenization of selected samples.

All polyesters and cellulose fibers were dried at 105°C for 24 h before compounding. Any possible moisture uptake by the fibers during feeding of the extruder was eliminated in the degassing zone of the machine (vacuum). The extruded strands were granulated before being injection-molded.

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.

Mechanical Testing

The test bars (DIN 53455), with a cross section of 10 × 3.5 mm and an effective length of 75 mm, were

conditioned at 23°C and 50% RH for 24 h before testing. The tangent modulus, E ; the stress at yield, σ_y ; and the corresponding elongation, ϵ_y , were determined from the stress-strain curves (Instron Model 1193, extensometer G51-15MA, deformation rate $4.5 \times 10^{-3} \text{ s}^{-1}$). The Charpy impact strength, IS , was measured on unnotched samples (Frank, Model 565 K, DIN 53455). The mechanical parameters were evaluated from data using at least 10 test bars for each composition and fiber content. Filling levels are given as weight percentages.

Dynamic Mechanical Properties

The dynamic mechanical properties were evaluated in the bending mode using a Rheometrics RSA 11 dynamic mechanical analyzer. The frequency of the forced oscillation was kept at 1 Hz.

Differential Scanning Calorimetry

Differential scanning calorimetry (Mettler TA 3000) was used to determine the melting points and the crystallinity of the polyesters and cellulose composites. The heating rate was 10°C/min.

Scanning Electron Microscopy (SEM)

The tensile fracture surfaces of the composite samples were studied with a Jeol JSM-350SM scanning electron microscope operated at 25 keV.

RESULTS AND DISCUSSION

The Effect of Composition on Mechanical Properties

Table III illustrates the effect on the tensile modulus of the incorporation of cellulose fibers into three

Table IV Mechanical Properties of Cellulose-Polyester Composites

Composition	Matrix	Tensile Modulus (GPa)	Elongation at Break (%)
PHB 40% cellulose	Polyhydroxybutyrate	6.21	1.07
PHB/6% HV 40% cellulose	Polyhydroxybutyrate/ 6% polyhydroxyvalerate	5.70	1.59
PHB/10% HV 40% cellulose	Polyhydroxybutyrate 10% polyhydroxyvalerate	5.01	1.71
PHB/15% HV 40% cellulose	Polyhydroxybutyrate/ 15% polyhydroxyvalerate	4.14	1.75

different thermoplastics: polypropylene (PP), polystyrene (PS), and polyhydroxybutyrate (PHB). The tensile modulus increased for each composite with an increased fiber loading. The stiffening effect of cellulose in PHB is in the same order as that of PS. Cellulose-reinforced PHB is strong and stiff, but also very brittle.

A series of copolymers (PHB/HV), composed principally of PHB together with varying proportions of hydroxyvalerate (HV) and incorporated randomly by bacteria throughout the polymer chain, were also selected as matrix for cellulose composites. Modification of PHB with HV resulted in a dramatic improvement in ductility. The results of measurements of the mechanical properties of the injection-molded PHB, PHB (HV) copolymers, and composites containing cellulose fibers are summarized in Table IV. An increased HV content in PHB yields polymers with a lower stiffness. Table IV also shows the effect of the fiber content on the tensile modulus for the composites with various matrix composition.

Table IV illustrates the effect of cellulose fiber loading on elongation at break, ϵ_b . As can be expected for filled polymers in general, the elongation at break decreased when cellulose was incorporated into PHB. The selection of polyester copolymers with an increased HV content as matrix resulted in com-

posites with increased elongation at break and an improved ductility, compared to cellulose PHB composites. This is also illustrated in Table IV. Injection molding of the tensile test bars containing 60% cellulose was limited by the high viscosity of the filled melts.

The Effect of Processing on Properties

An important feature of the molded samples is the degree of dispersion of the fibers in the matrix and the overall homogeneity of the composite structure. We have compared three different compounding techniques used for mixing cellulose fibers with the matrix material: Buss-Kneader, a twin-screw extruder, and Brabender. Selecting the proper processing method gave a highly significant improvement in this respect. Compounding the fibers with polyester in the Brabender resulted in an excellent dispersion of cellulose and better homogeneity than one-step compounding in the extruders.

We also investigated the effect of compounding techniques on fiber length. To determine the L/D ratio, parts of the molded test bars were dissolved in hot chloroform. The solutions were filtered, and the fibers retained on the filter were washed with hot chloroform and dried. The size of the fibers was

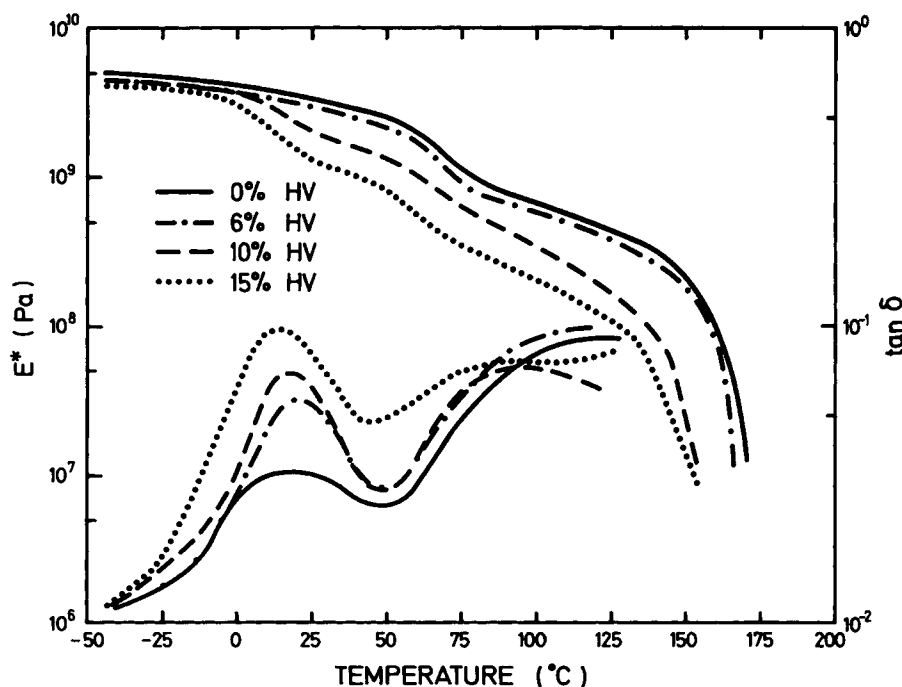


Figure 1 Dynamic mechanical spectrum of PHB and PHB/HV copolymers with various HV content. Lower curves show $\tan \delta$ as a function of temperature; upper curves show E^* as a function of temperature.

determined microscopically. The average fiber length, which was independent of the fiber loading, was 200, 104, and 60 μm for fibers compounded in the Buss-Kneader, the twin-screw extruder, and the Brabender, respectively. The initial average cellulose fiber length was 1.1 mm. The fiber attrition during compounding is thus significant and strongly dependent on the compounding process used. This also affects dispersibility.

Crystallinity

The PHB homopolymer is a completely stereoregular polyester, and it is therefore capable of achieving high levels of crystallinity. The mass fraction crystallinity of a typical PHB sample left to crystallize fully for several weeks at a temperature above its glass transition is in the range of 60–90%.¹⁸ In our study, no attempts were made to anneal samples. However, all samples have the same thermal history. Crystallinity in pure polymers and cellulose composites was determined by the use of DSC measurements. The heat of fusion of 146 J/g was used for calibration. Copolymers with an increased HV content have, as expected, a lower crystallinity. Introducing cellulose, however, does not affect the degree of crystallinity.

Dynamical Mechanical Properties

The dynamic mechanical properties of polyesters with various compositions and cellulose composites were studied over a wide temperature range (-50 to 200°C). Figure 1 shows the storage modulus E^* and the mechanical loss factor $\tan \delta$ for the unfilled polyesters. The peak representing the mechanical loss factor passes through a maximum in the temperature range of 0 – 25°C , which corresponds to the glass transition. As expected, the increased HV content in the copolymer decreased the degree of crystallinity, which then resulted in an increased mechanical loss factor, $\tan \delta$. The α -peak also tends to shift to a lower temperature with an increased fraction of the amorphous phase in the copolymer.

Another relaxation at 80 – 90°C is observed for PHB and its copolymers. This relaxation, called α_c -dispersion, is attributed to molecular motion within the crystalline phase.¹⁹ The upper curves in the DMTA spectra represent the dynamic modulus, E^* . Increasing concentrations of HV in the copolymer result in a lower dynamic modulus as well as the greater decrease in the dynamic modulus with increasing temperature. This is an expected consequence of a lower crystallinity.

Dynamic mechanical spectra recorded for 40%

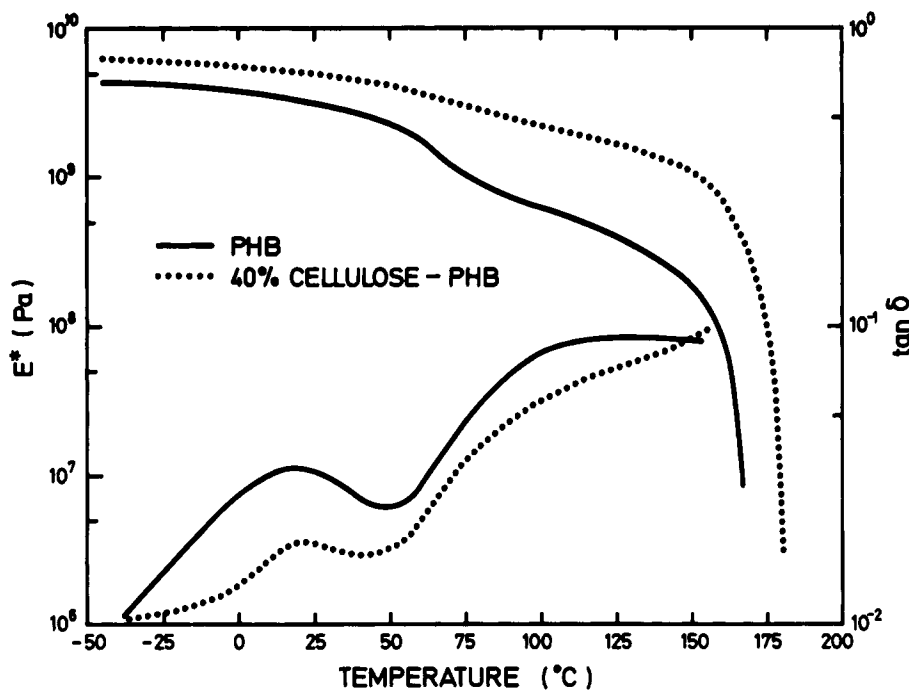


Figure 2 Dynamic mechanical spectrum of PHB and 40% cellulose-PHB composite. Lower curves show $\tan \delta$ as a function of temperature, upper curves show E^* as a function of temperature.

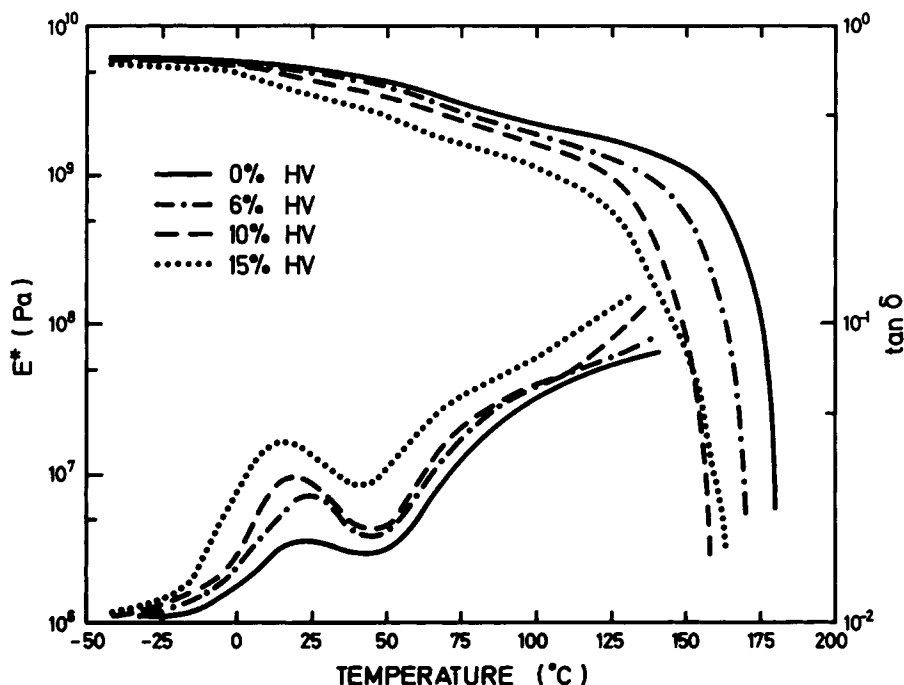


Figure 3 Dynamic mechanical spectrum of 40% cellulose-PHB/HV composites with various HV content. Lower curves show $\tan \delta$ as a function of temperature, upper curves show E^* as a function of temperature.

cellulose PHB composite were compared with spectrum recorded for an unfilled PHB in Figure 2. The introduction of cellulose did not affect the glass transitions of the matrix, as observed by the unchanged positions of the loss modulus maxima. However, the loss factor, $\tan \delta$, is strongly affected by the presence of cellulose. The α -peak is much smaller for cellulose PHB composites, which is characteristic normally for an increased crystallinity. As the degree of crystallinity was not affected by introducing cellulose into the polyester matrix, a decrease of the loss factor bears witness to restrictions in the mobilities of the chain segment in the amorphous phase as a result of the presence of a cellulose phase. The addition of cellulose shifts the dynamic modulus to higher values over the entire temperature range measured. The improvement of stiffness is especially significant at elevated temperatures, which is beneficial because of the limitation of heat-sag.²⁰

The dynamic mechanical properties of 40% cellulose and polyesters with various HV contents are shown in Figure 3. The reduction of the loss factor owing to the incorporation of cellulose in PHB is compensated by an increased volume of the amorphous phase in composites with matrices having a

higher HV content. In fact, damping, expressed as loss factor peak, is higher in 40% cellulose composite with PHB (15% HV) as the matrix than in pure PHB. The composite having a composition such as this shows a higher stiffness over the entire temperature range as compared with unfilled PHB polymer.

Interfacial Properties

Interfacial properties of cellulose-polyester composites were investigated using scanning electron microscopy. Figure 4 shows an SEM micrograph of the tensile fracture surface of 40% cellulose-PHB composite. Very good dispersion is evident. No fiber bundles or aggregates are observed. Figure 5 shows a selected area at higher magnification. A good distribution of fibers and good wetting are seen. The ruptured cellulose fibers present on the fracture surface are evidence of good interfacial adhesion between cellulose fibers and bacteria-produced PHB.

Interfacial properties of cellulose composites with copolymers with various compositions were also investigated. Figures 6 and 7 show the fracture surfaces of 40% cellulose-PHB (6% HV) and 40% cellulose-PHB (15% HV). The degree of fiber distribution in

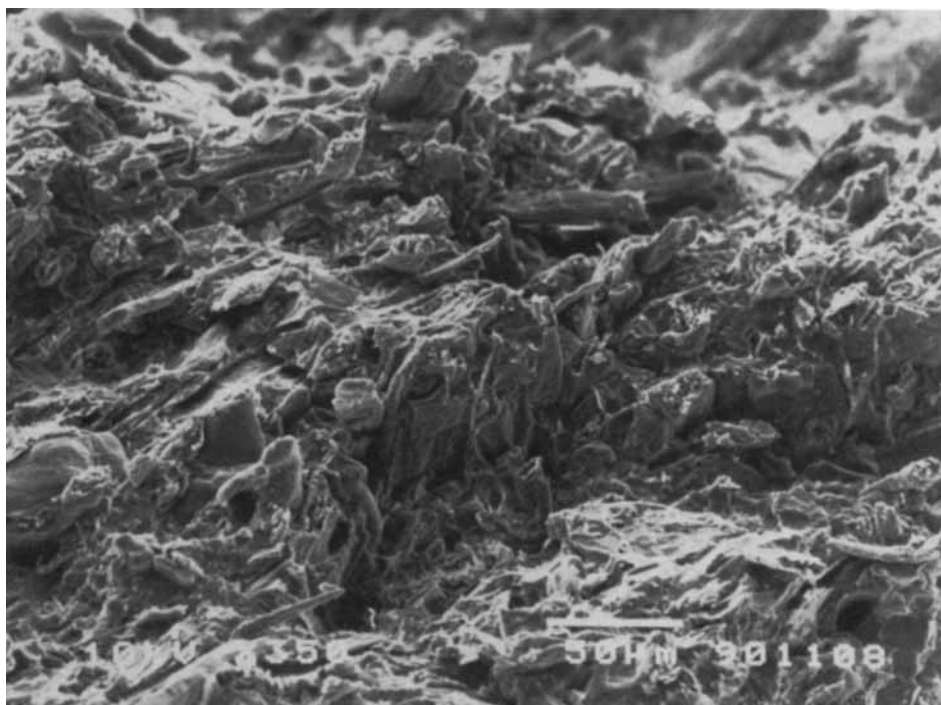


Figure 4 SEM micrograph of fracture surface of 40% cellulose-PHB composite (magnification $\times 350$).

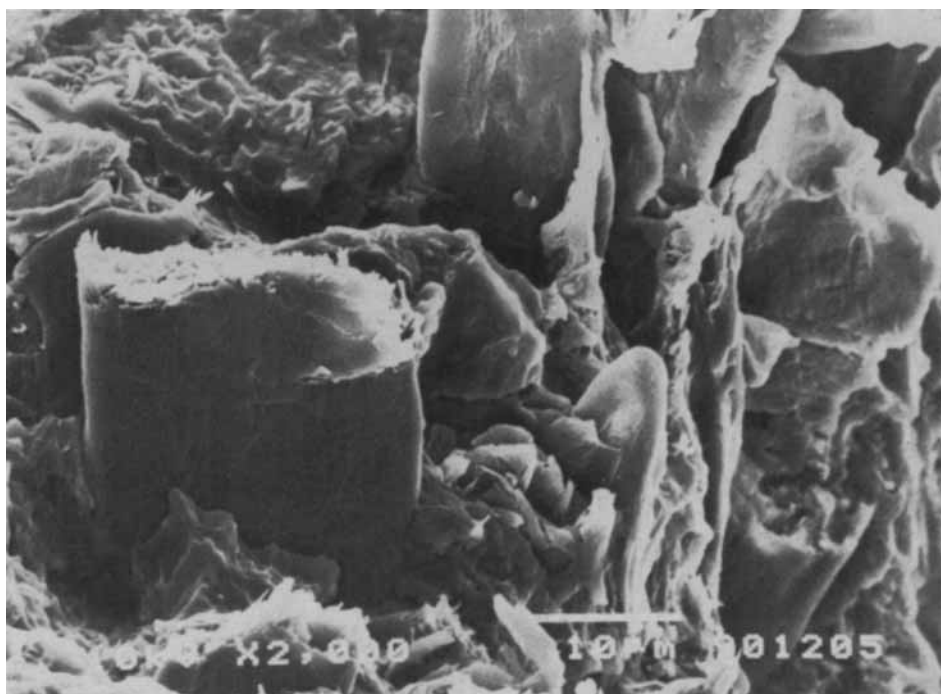


Figure 5 SEM micrograph of fracture surface of 40% cellulose-PHB composite (magnification $\times 2000$).

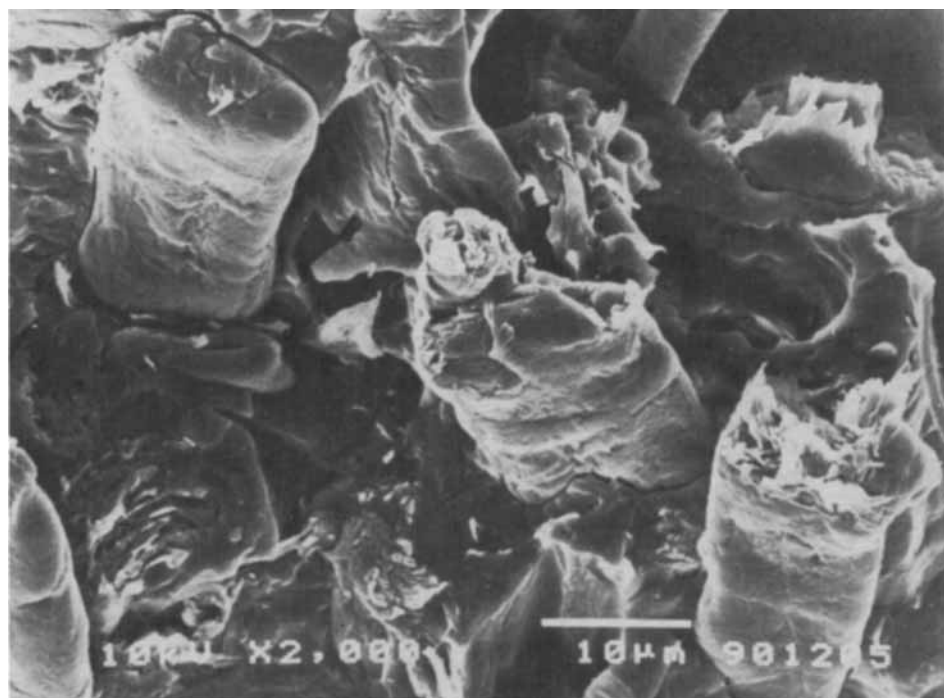


Figure 6 SEM micrograph of fracture surface of 40% cellulose-PHB (6% HV) composite (magnification $\times 2000$).

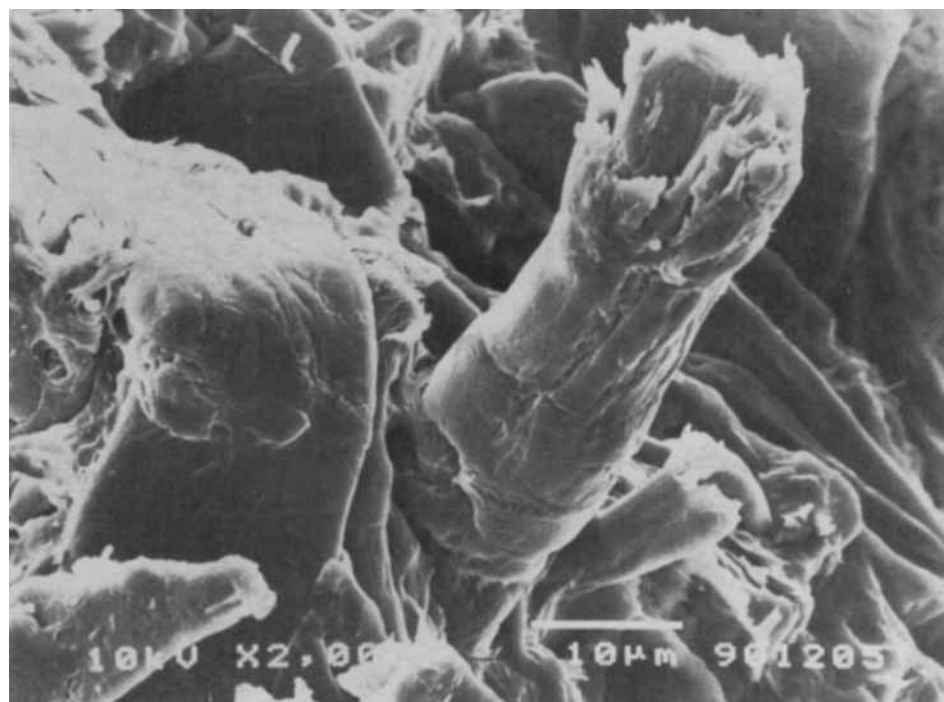


Figure 7 SEM micrograph of fracture surface of 40% cellulose-PHB (6% HV) composite (magnification $\times 2000$).

the matrix is similar to that of the PHB composite. The length of the fiber that has been pulled out before rupture is gradually increased with an increased HV content of the copolymer. The fiber pullout with a following fiber rupture is a result of the increased ductility of the matrix and contributes to the impact strength of a composite and a higher elongation at break.

Dispersibility

One of the unexpected but very desirable properties of cellulose bacteria-produced polyesters is the excellent dispersibility of the cellulose phase in the polyester matrix. One explanation for this apparent compatibility between cellulose and polyesters could be the fact that PHB and its copolymers are able to partake in many of the hydrogen-bonding types of specific interactions. The miscibility of polyesters with chlorinated polymers, polyamides, functional polymers, and cellulose derivatives is well documented.²¹

As is evident from our earlier studies, introducing cellulose fibers into thermoplastic matrices such as PP or PS produces composites with very low impact strength levels even at relatively low (20%) fiber contents.⁷ The reason appears to be the uneven dispersion of the fibers and their fragments in the matrix. The impact strength was significantly improved by cellulose fiber hydrolysis and the addition of compatibilizing and coupling agents.¹⁴

Another possible explanation for the excellent dispersibility combined with the high impact strength of cellulose-polyester composites would be fiber attrition during processing. We observed in our earlier studies that, for the hydrolyzed fibers, the fiber length reduction was desirable, the ideal situation being the conversion of all fibers into microfibrils.

Degradation during Processing

Melt instability of PHB and its copolymers owing to thermal degradation is well documented.²² The thermal stability of pure polymers and cellulose-filled composites was investigated with thermogravimetric analysis (TGA). Figure 8 shows complete weight loss in a single step between 225 and 250°C, corresponding to the quantitative conversion of PHB to crotonic acid. The presence of cellulose does not affect the degradation process. However, it is plausible that processing cellulose with PHB in the Brabender at 190°C induces a local overheating. If

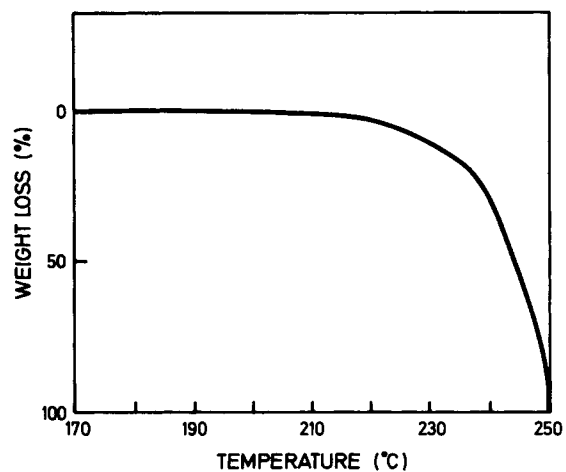


Figure 8 TGA thermogram for PHB. Weight loss vs. temperature.

crotonic acid is developed, the cellulose fibers could possibly be hydrolyzed in such conditions. This would explain the fiber-length reduction reported in an earlier section. Fibers extracted from samples compounded in the Brabender, and which have not been loaded, were investigated with SEM. Figure 9 gives clear evidence of fiber breakage, which is not a common result of mechanical processing of cellulose with polymers alone. The cellulose fibers show defibrillation, which is characteristic for hydrolytical treatment. We suggest, on the basis of our experimental observations, that fiber hydrolysis is occurring, owing to the crotonic acid action. Work is continuing in our laboratories to systematically investigate a degradation process of polyester and following *in situ* hydrolysis of cellulose in the processing step.

CONCLUSIONS

Novel materials composed of bacteria-produced polyester reinforced with wood cellulose fibers were manufactured and their properties investigated. First, the incorporation of cellulose in PHB was compared with the incorporation of cellulose in synthetic polymers. The mechanical properties of cellulose-PHB composites were similar to those of cellulose-synthetic polymer composites. This included high stiffness, but also brittleness. A reduction of elongation at break was compensated by selecting polyester matrices with an increased HV content. Such polymers are also produced by bacteria when propionic acid is added to the nutrients.

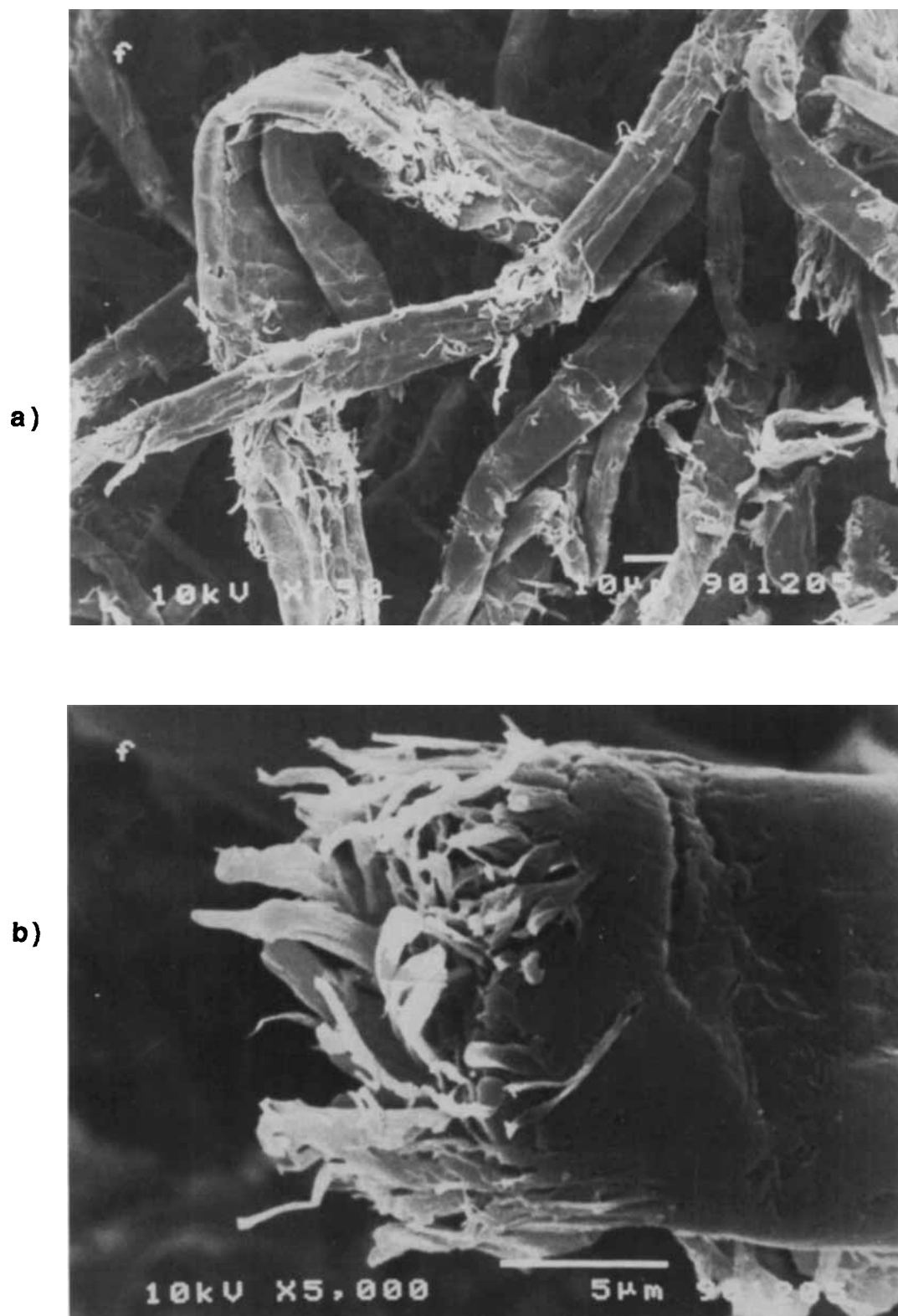


Figure 9 SEM of cellulose fibers extracted from unloaded samples: (a) magnification $\times 750$; (b) magnification $\times 5000$.

Cellulose-PHB composites showed a high degree of homogeneity and excellent dispersion of cellulose in the polymer matrix. This was strongly dependent on processing conditions and related to a significant fiber-length reduction. A microscopic investigation of fiber extracted from samples shows defibrillation characteristic for hydrolytic treatment. We therefore believe that partial hydrolysis of cellulose is taking place during the processing. This is likely to be induced by crotonic acid, which is formed as a result of the thermal degradation of polyester.

In summary, we find that incorporation of the cellulose fibers greatly improved the mechanical properties of bacteria-produced polyesters. An excellent dispersion of fibers was achieved. The cost of the resulting materials is very attractive as compared with the rather expensive matrix and yet the material is still biodegradable.

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