Film formation and paper coating with poly (β–hydroxyalkanoate), a biodegradable latex

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ABSTRACT: An aqueous latex of a poly (β–hydroxyalkanoate) (PHA) coated on paper imparted water imperviousness without changing mechanical properties. Hot–pressed films biodegraded faster than solvent cast films. The PHA coating on paper degraded totally in activated sludge within 12 days, leaving the cellulose matrix relatively untouched. Blends of PHA latexes with sodium carboxymethyl cellulose, polystyrene latex, carboxylated styrene/butadiene latex, natural rubber latex, and starch powders form satisfactory films at room temperature.

KEYWORDS: Biodegradability, coating, film, formation, latex, mixtures, paper, starch, water permeability.

The purpose of this work was to assess the film forming characteristics and biodegradability of poly (β–hydroxybutyrate) (PHB) and poly (β–hydroxybutyrate co–valerate) (PHB/HV) concentrated native granule suspensions or latexes. We demonstrate their use as films, coatings, and composites as well as blended with other polymers. There is particular emphasis on paper applications where synthetic, nonbiodegradable latex finds extensive use. Our findings have broad applications to the whole family of PHA. We will therefore refer to this family, although most of our work concentrated on PHB and PHB/HV latexes.

Preservation of the nascent state and granular morphology of the polymer depends on the separation procedure of PHA from bacterial cells. **Table I** shows the three major approaches to PHA isolation: solvent extraction, chemical digestion, and selective enzymolysis. Compared to solvent extraction, the other two methods preserve the granular morphology of PHA. They are therefore suitable for latex production. Both chemical and enzymological approaches consist of selective digestion on non–PHA components. The chemical procedure (*1*) involves pretreatment of the biomass with detergent and subsequent washing of the residue with sodium hypochlorite at pH 13. One must carefully control the process to avoid degradation of the PHA by hypochlorite oxidation.

Selective enzymolysis is similar to chemical digestion except that enzymes such as proteases and deoxyribonuclease hydrolyze the unwanted biomass components. Since these enzymes act with much greater specifiity than chemicals such as hypochlorite, the recovered granules should bear a closer resemblance to their native state in the microbial cytoplasm. There are commercial applications of this method presently in operation (*2, 3*). Research laboratories have made extensive use of similar techniques to prepare "freshly isolated" granules with disruption of cell walls by lysozyme treatment followed by sonication. Centrifugation allowed subsequent recovery onto a bed of glycerol (*4*).

Enzymatic isolation of PHA granules partially preserves the original molecular organization of the polymer chains. Films from suspensions of such granules should possess properties different from those of solvent–extracted PHA as long as the film processing conditions are at temperatures less than the melting temperature. Starch is an example of a hydrocolloid where commercial isolation processes pre-

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serve the original structure. Starch undergoes reversible cycles to reform a crystalline hydrate after each dehydration. Starch gelatinization with steam irreversibly destroys its structure. By contrast, PHB and PHB/HV native granules are noncrystalline in their original form. Isolation and drying provokes crystallization and thereby changes irreversibly the film forming properties of the original particles (*5*).

Recent studies (*6, 7*) on the morphology of isolated granules have established that a crystalline shell invariably develops at the surface of the granules after isolation from the cytoplasm. The texture of this crystalline shell corresponds to single, lamellar crystals. This topotactic shell surrounds a noncrystalline core whose mobile properties are discernable from high-resolution nuclear magnetic resonance methodology (*8*).

I. Survey of PHA isolation processes

Isolation process	*Procedure*
Extractive solvents: solvent extraction of PHA	a. Pretreatment with acetone to remove water and polar lipids
	b. Chloroform extraction of PHA followed by precipitation into methanol
Chemical digestion: selective for non–PHA components	a. Pretreatment with detergent to solubilize lipids and protein
	b. Washing of residue with sodium hypochlorite at pH 13
Biochemical digestion: granule isolation after selective enzymolysis of biomass	a. Flash steaming to lyse cells and denature DNA
	b. Sequential enzyme treatments for removal of insoluble macromolecules

Experimental

Latex sources

We obtained latex samples from a commercial source or prepared them ourselves. The term latex refers to an aqueous suspension of PHA granules never subjected to drying. We isolated the original granules from *Alcaligenes eutrophus* by an enzymolysis process (*2*) or by chemical treatment of the biomass using a detergent–hypochlorite process (*1*). In both we did not dry the granules. We repeatedly washed the isolated granules with water and concentrated them to between 20% and 50% solids on a weight basis. Both the biochemical and chemical methods produced a latex of similar purity. They contained about 95% PHA and retained the granular morphology. The latex samples in this study were the following:

- PHB homopolymer
- PHB/HV copolymer isolated by the hypochlorite process containing 5.5%, 7.5%, and 11% HV
- Twenty-one percent and 27% HV copolymer samples obtained commercially.

The copolyesters of PHB/HV indicated above are random copolymers (*9, 10*).

Film forming techniques

We cast the latex suspensions at 15–20% solids on an impervious substrate such as glass or polyester to prepare films. Drying the cast suspension at room temperature produced a "cake-like" structure with poor mechanical properties. Subsequent hot-pressing converted this structure into a transparent, flexible film. Hot–pressing used a laboratory press at 5000 psi for 1 min at a temperature always below the melting temperature of the dry polymer. Depending on the HV content, these temperatures ranged from 100°C to 140°C. This was the minimum requirement for complete formation of a dense film. Hot–pressed films were crystalline by X–ray diffraction but nonspherulitic in a polarizing microscope.

There was an intermediate state of coalescence when heating the air-dried latex "cake" of 21% and 27% HV materials at 130°C for 10 min. These films were white, opaque, porous, and peelable from the casting surface. Scanning electron microscope (SEM) views of these films, shown in **Fig. 1**, indicated a three-dimensional array of 0.5–1.5-μm spherical particles or granules partly coalesced with interparticle capillaries of 0.16-μm radius. **Figure 2** clearly shows the particulate nature of the starting latex (*5*).

Films cast from freshly isolated PHB granules (*4*) using hot–pressing at 5000 psi and 135°C were nonspherulitic but showed large domains of birefringence in the polarizing microscope as if shear stresses were frozen inside the films. Their degree of crystallinity, determined by powder X–ray diffraction seen in **Fig. 3**, was much higher than that of the films isolated chemically or from enzymolysis.

We dissolved PHB and PHB/HV powders in chloroform to make solvent cast films. We cast these solutions on glass or polytetrafluoroethylene (PTFE) at room temperature or 40°C to evaporate the solvent. These films showed the expected high extension to break for films with spherulitic texture (*11*). The films aged for two weeks to allow them to reach equilibrium crystallinity (*12*). Solvent casting destroys the original morphology of the granules.

We prepared films with clarity and toughness similar to plasticized cellophane by vapor coalescing air dried, cake–like latex films. We exposed them to solvent vapors for a period of 24 h in

a desiccator. Chloroform vapors produced extremely smooth, flexible, and tough films that were transparent and conformable on drying. They showed X-ray crystallinity but were not birefringent.

Latex coated paper

We made latex coated paper using unconditioned basestock paper strips of 40 g/m^2 basis weight with a 1:1 mixture of mechanical and chemical pulp. We used a 20% solids content latex dispersion to coat paper strips by hand with a set of contoured metering rods. The coatings were flexible, coherent, and adhesive to paper even when dried at room temperature. Adhesion of latex particles to paper substrates depends on conformability of the latex to drying stresses. This is quite favorable in the case of a latex which has not undergone drying. On the other hand using reconstituted latexes made by dispersing commercial spray-dried PHA powders in water to coat paper strips produced coatings which did not adhere to paper because of the higher crystallinity of the granules.

Hot-pressing between polyester sheets of coated paper samples used 5000 psi at temperatures ranging from 100°C to 140°C, depending on the copolymer composition, for 1–2 min. The latex coating fused and adhered to the paper. The coated surface was transparent and glossy after the hot-pressing.

Results and discussion

Mechanical properties

Table II lists the physical and mechanical characteristics of latex coated sheets according to standard paper tests. The tearing behavior of PHB and PHB/HV coated paper was almost the same as the basestock. Polyolefin coated papers using melt extrusion do not tear in the same manner. In that case the paper tears first, leaving a plastic film that trails and necks to 100% elongation or more. Hot-pressed PHA coatings were not peelable from paper substrates. Overall the PHB or PHB/HV coatings did not significantly change the mechanical properties of the basestock.

Wetting and barrier properties

Water is the most important liquid to consider for wetting of PHA films. The measured value of contact angle θ between PHA latex film and water (*5*) was about 72°. For comparison, the contact angles of polyester and nylon with water are 71° and 65°, respectively. Polyethylene and PTFE have values of 95° and 112°, respectively (*13*). PHB is therefore a polar material which water will wet. Indeed, PHB will wick water, if it is in the form of a microporous network.

We measured water vapor transmission rate (WVTR) on samples of PHA coated paper prepared by a direct electrostatic powder coating technique (*14*). This novel coating method deposits the spray dried powder directly onto paper with subsequent fusing and pressing under similar conditions to those described above. The WVTR values for the PHB/HV electrostatically coated paper were higher than the values of polypropylene (PP) coated paper prepared under the same conditions for comparison purposes. This is normal for a more polar polymer. **Figure 4** provides the plot of WVTR at varying coating weights for PHB/HV with 8.1% HV and PP. It shows a pattern similar to those of binary composite laminates (*15*). Poor barrier properties at low coating weights are due to penetration of the cellulose fibers through the polymer film. After exposure to moisture, these fibers wick water through the polymer film. Increasing the coating weight gave a steady decrease of the permeability values. The observed permeability rate of coated paper approached the value of the polymer film for coating weights exceeding 40 g/m^2.

Microbial degradation

This study used hot-pressed PHB/HV latex films and PHB and PHB/HV latex coated hot-pressed paper samples. The polymer films varied in thickness from 0.08–0.09 mm to 0.2 mm. The study also contained chloroform cast films made with bacterial PHB to assess the influence of film morphology upon the rate of degradation. Other researchers detail the procedure to evaluate the degradation of test specimens exposed to a microbial environment of simulated activated sewage sludge (*8*).

The PHB/HV with 21% HV hot-pressed latex films showed a steady weight decrease over a period of 12 days leading to the total weight loss of 83% shown in **Fig. 5**. The SEM of **Fig. 6** showed the erosion of the film surface as a result of bacterial attack.

In a separate experiment, paper coated with PHB latex lost 35% of its initial weight after 12 days. This corresponded to almost the entire coating weight of the sample. SEM examination of the surface of PHB coated paper after 12 days of incubation (**Fig. 7**) showed that the weight loss was due to the biodegradation of the PHB layer, since the cellulosic fiber support remained intact.

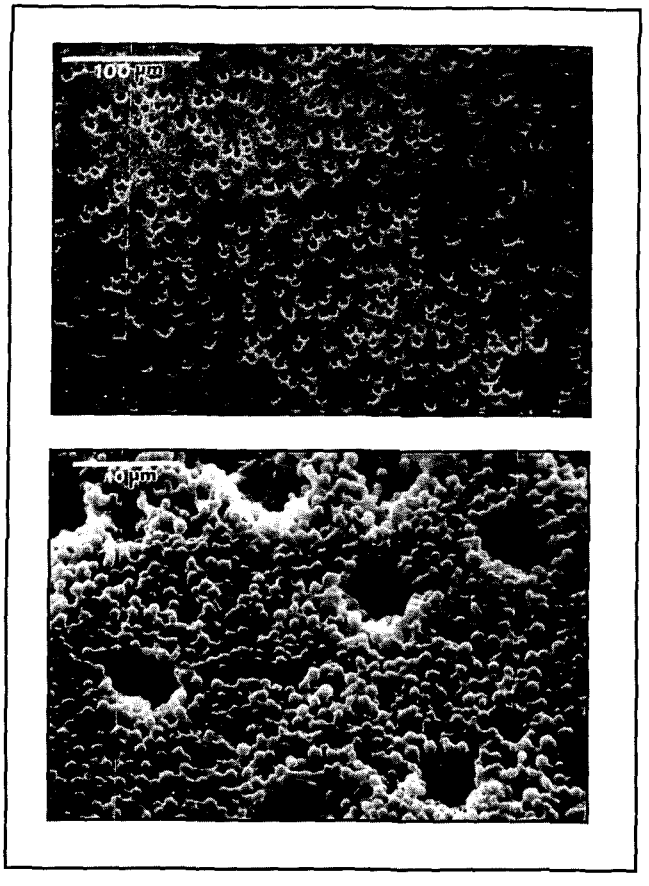
Filmmaking technique affects the rate of PHA biodegradation. Hot-pressed latex films degraded faster than solvent cast films. An explanation is the loss of the granular morphology of the original PHA granules due to the dissolution and casting of the polymer compared to the hot-pressing technique (*12*).

To assess the influence of the copolymer HV content upon film biodegradability, we determined the rate of degradation by activated sludge for two copolymer compositions of 5% and 11% HV after eight days exposure. There was no clear evidence that the degradation rate corresponded to the HV content in the copolymer PHB/HV.

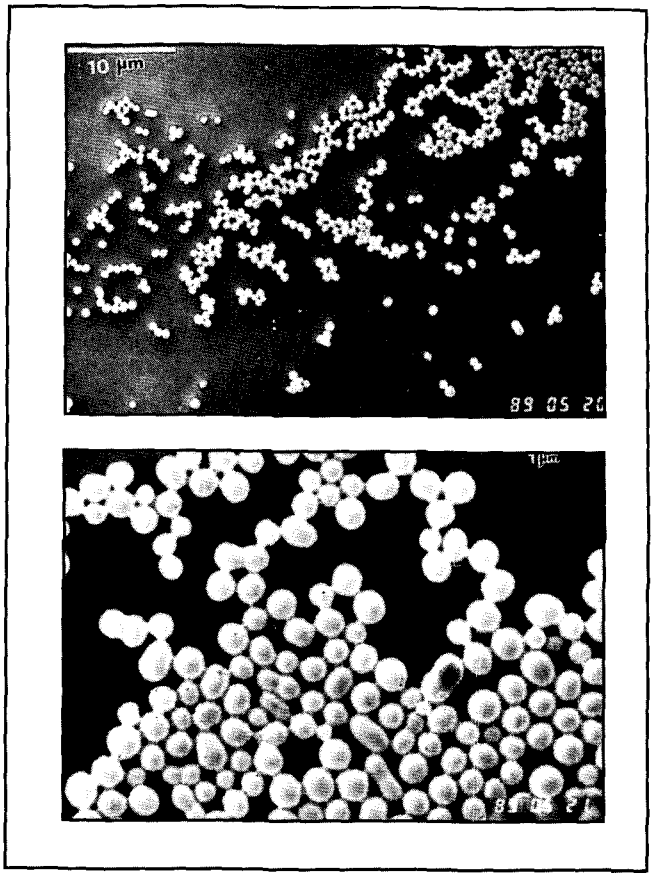
PHA latex formulation

Film forming and coating applications of PHA latex may require formulation and blending to obtain the necessary properties. Paper applications and the production of PHA composites require blending with inorganic pigments, plas-

1. Two views of PHB/HV film with 21% HV made by air drying a 20% solids latex suspension followed by heating at 130°C for 10 min



2. Two views of SEM of PHB granules using spray dried powder suspended in distilled water and treated by ultrasound for 1 min prior to deposition on the support for observation



tic pigments and binders made from synthetic polymer latexes, and other biopolymers such as starch or cellulose and its derivatives.

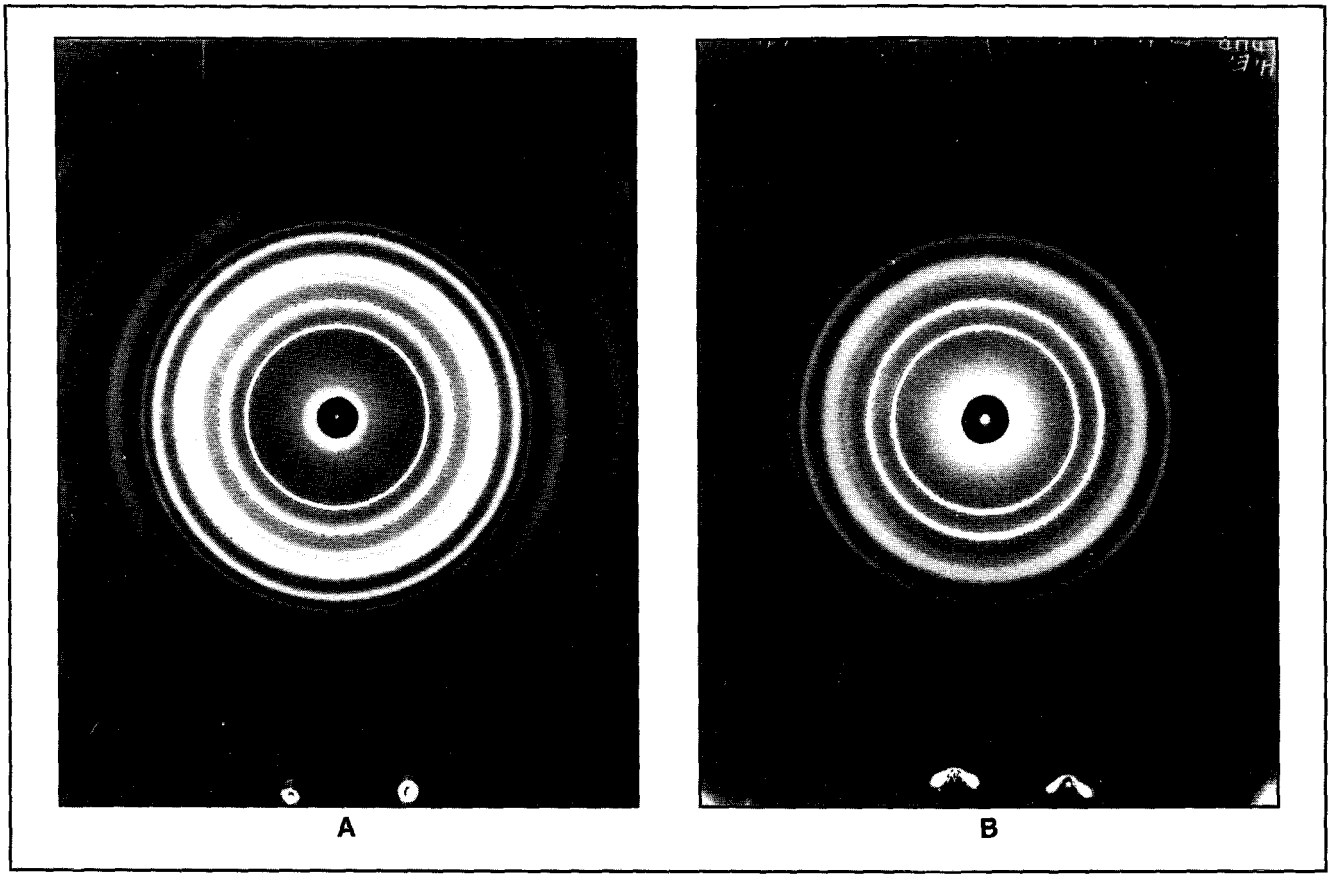
In a preliminary study, we blended PHB and PHB/HV latexes with sodium carboxymethyl cellulose (CMC), polystyrene latex, clay, carboxylated styrene/butadiene latex, natural rubber latex, hybrid starch with 70% amylose, and cross-linked potato starch. We prepared the blends by mixing the two components at 25%, 50%, and 75% weight ratios and stirring the resulting mixture at low shear to produce a uniformly dispersed phase. Some cases required water addition to improve dispersion. We cast the films as before, allowed them to dry at room temperature overnight, and subsequently hot-pressed them for 1 min at 5000 psi and at a temperature in the range necessary to fuse an unblended polymer film (100–140°C). It is possible to mix PHA latex never subjected to drying with all the materials mentioned above without phase separation at room temperature. In the case of PHA with natural rubber and PHA with carboxylated styrene/butadiene latex blends, colloidal compatibility did not translate into a uniform film after drying. The two components segregated to yield the PHA component on the casting substrate covered by a rubbery film. Hot-pressing of air-dried cast latex blends of PHA with carboxylated styrene/butadiene, using less than 25% carboxylated styrene/butadiene, produced uniform films. This implies dispersion compatibility of the two components.

Mixing starch granules with PHA latex gave films with good characteristics. There were mixtures of PHB/HV latex (both 5.5% and 27% HV) and 65% amylose content starch powder in 25%, 50%, and 75% ratios. Hot-pressing air-dried cast blends of 1:1 PHA/starch produces films where

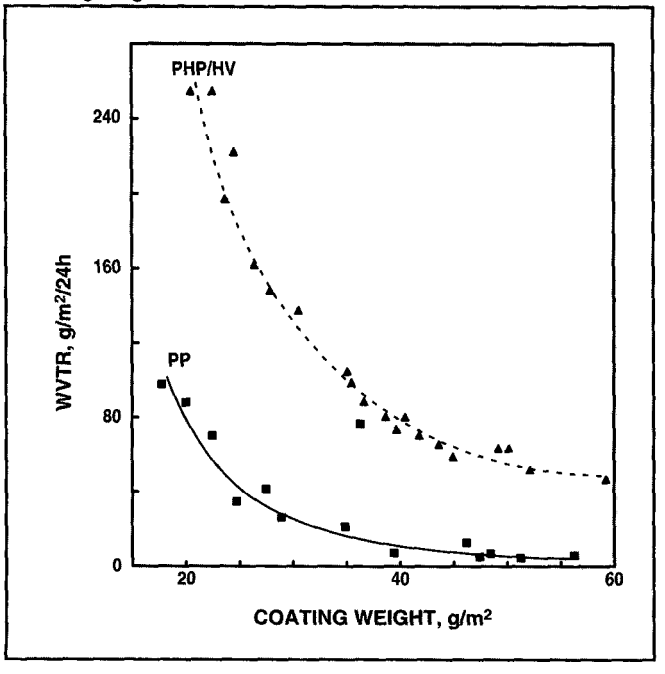
II. Physical and mechanical characteristics of PHB and PHB/HV latex coated paper

Characteristic	*PHB*	*PHB/HV*	*Base stock*
Basis weight, g/m²	48.0	74.0	37.4
Burst index, kPa·m²/g	0.90	1.65	2.31
Breaking length, km	4.75	5.10	6.85
Stretch, %	0.95	2.10	1.59
Tensile index, N·m/g	46.30	50.20	67.16

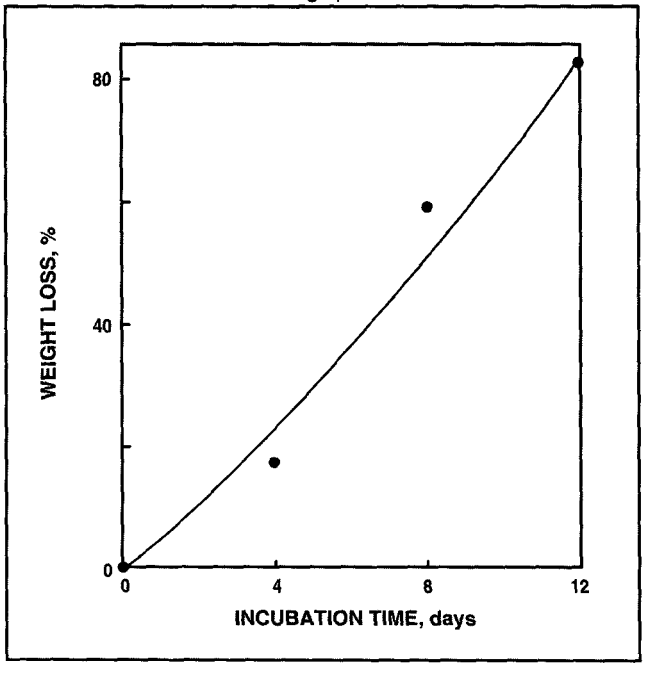
3. Wide-angle X–ray pattern of latex films made by hot pressing at 135°C and 5000 psi for 1 min from PHB granules isolated with enzymes in our laboratory (A) and by a chemical approach (B)



4. WVTR of PHB/HV with 8.1% HV and PP coated paper as a function of coating weight at 37.8°C and 95% RH



5. Microbial degradation of hot–pressed PHB/HV latex film with 21% HV in a simulated activated sludge process



starch granules are embedded in a continuous PHA phase in such a way that overnight immersion in water at room temperature does not affect the resulting material. Experiments are under way to characterize further the exact morphology of such films. They appear to be a uniform dispersion of starch granules in a PHA matrix (*16*).

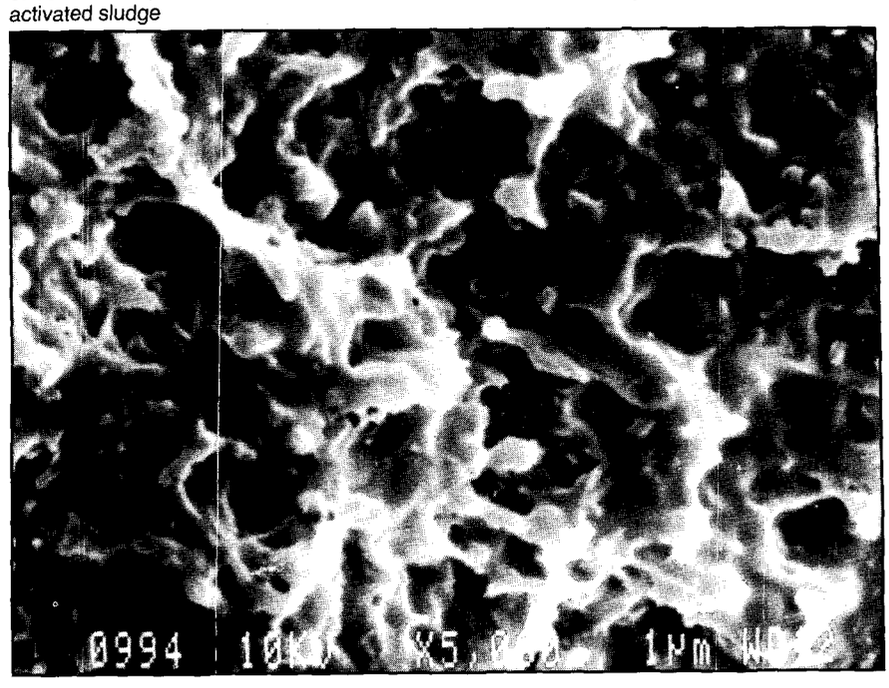
Conclusions

From a polymer morphology perspective, the most notable result in this study is the nonspherulitic character of the hot-pressed PHA films. They are flexible, but their extension to break is almost like that of paper. This suggests a limitation in chain entanglement of the interparticle surface. There also is a strong element of original morphology still present inside particle domains.

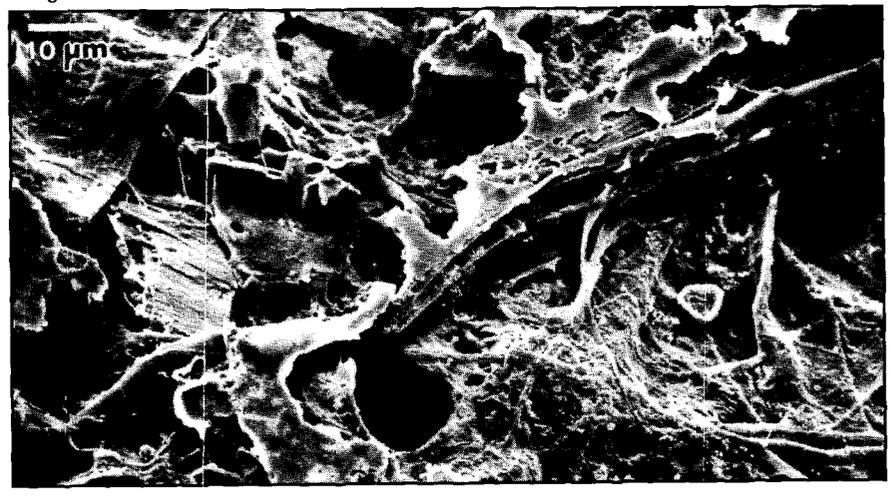
The lack of particle coalescence on drying at room temperature relates to the core and shell character of the granules in the dispersion (*6*). During isolation, surface crystallization occurs. Conformability to surface tension forces that draw the particles together does not occur unless drying temperatures are close to the melting temperature of the crystalline PHA. The crystalline nature of this shell and the rate and quality of the crystallinity that develops in the core on drying are under study. It is clear, however, that latex films of PHA require heat and pressure to produce a level of sintering to make an acceptable film from a barrier point of view.

The use of the enzymatic isolation process and the presence of HV in the polyesters are not limiting requirements to produce nonspherulitic, translucent, flexible polymer films from PHA latex. Films made of granules purified by the detergent–hypochlorite process had comparable toughness. The other desirable properties described above were not present in the solvent extracted or previously dried materials. All results seem to indicate the importance of processing the material in its never-dried latex state for film forming applications.

6. SEM of hot-pressed PHB/HV latex film with 21% HV after 12 days immersion in simulated activated sludge



7. SEM of hot-pressed PHB latex coated paper after 12 days immersion in simulated activated sludge



In particular, the ready sorption of the PHA latex by fibrous materials such as paper or nonwovens suggests applications such as binder, coating, or barrier. These applications in fibrous constructions become attractive when one considers the natural biodegradability of PHA (*17*).

From the applications point of view, PHA latex blends could offer advantages in the economics of PHA use. Blends with a synthetic film forming latex such as carboxylated styrene/butadiene could improve the toughness of PHA but with some sacrifice in total biodegradability. Alternately, blends with starch would maintain total biodegradability with substantial lowering of material costs. Clearly the latex state offers a unique opportunity for creating these particulate blends.

The particle coalescence character-

istics of these PHA latexes are poor compared to a natural rubber latex in spite of the ^{13}C nuclear magnetic resonance evidence that most of the granules of PHA are in a noncrystalline state before drying (*17, 18*). Drying the spread latex at temperatures close to the melting point of PHB or PHB/HV can overcome the lack of particle coalescence on drying at room temperature. Exposing the films to solvent vapor would further improve their optical homogeneity.

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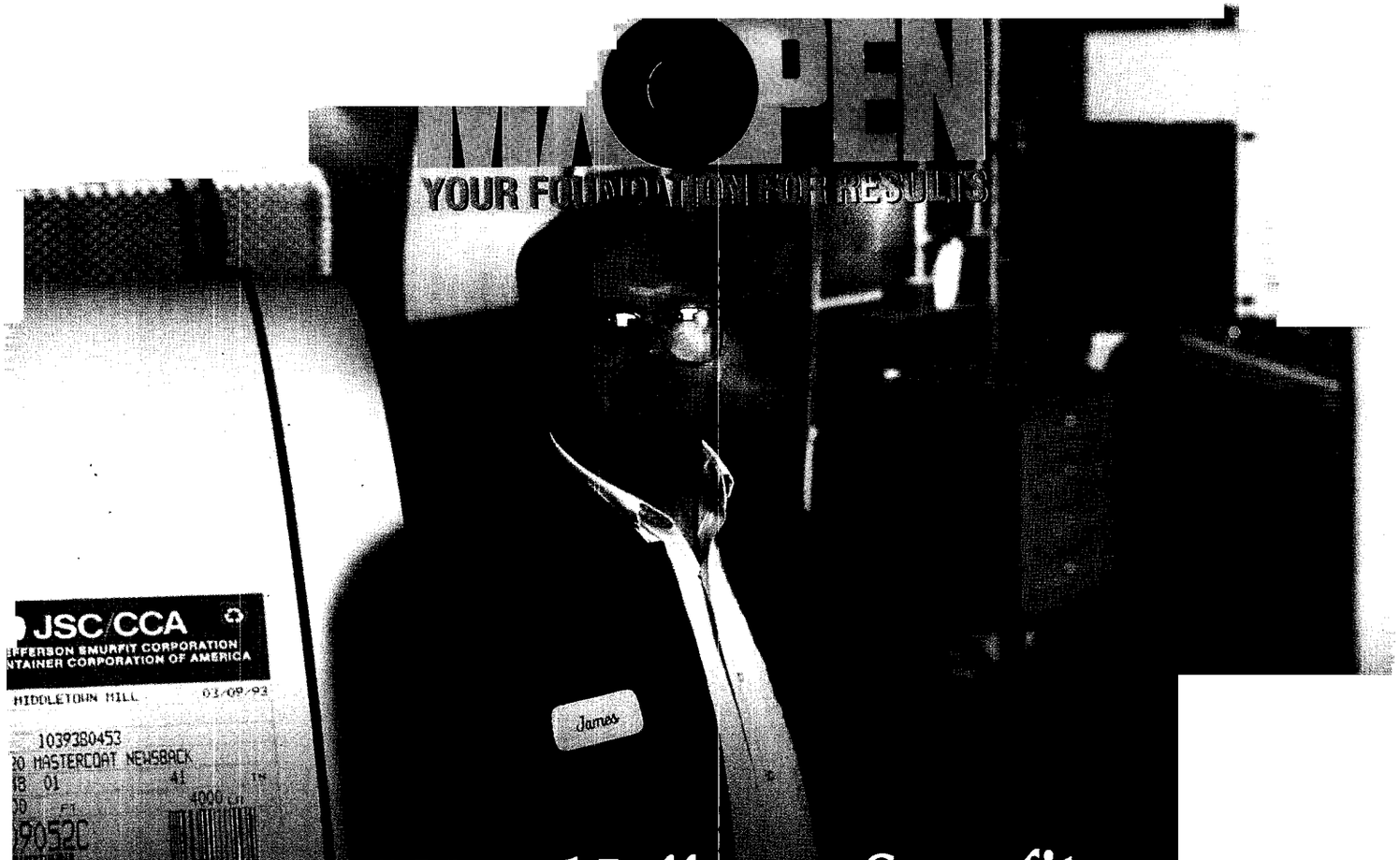

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