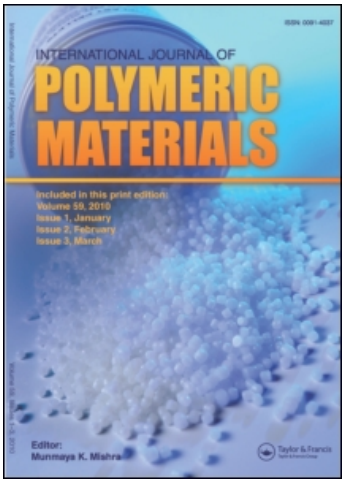

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Mechanical and Physical properties of chitosan and whey blended with poly(ε-caprolactone)

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MECHANICAL AND PHYSICAL PROPERTIES OF CHITOSAN AND WHEY BLENDED WITH POLY(ε-CAPROLACTONE)

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Properties important for packaging were studied on blends of 0–15 wt% poly(ε-caprolactone) and chitosan and a whey-protein-isolate. The blends were obtained by solution mixing, and films were produced by solvent casting. Transparency was measured by UV/VIS spectroscopy and the printability was qualitatively estimated by using a red ethanol dye. Mechanical properties of solid films and seals were assessed by tensile tests. Stiffness and folding endurence were also measured. The blend morphology was characterized by scanning electron microscopy. It was found that all the blends were transparent. The whey-protein-isolate had the best printability properties and printability remained in the poly(ε-caprolactone)-blends. Film stiffness decreased and strain at break increased strongly when the pure chitosan and the pure whey-protein-isolate were wetted. The addition of poly(ε-caprolactone) to chitosan and whey-protein-isolate had only a moderate effect on the toughness properties but a strong effect on the modulus, which could be predicted by the Halpin-Tsai model. The modulus of the whey-protein-isolate increased and the modulus of the chitosan decreased with the addition of poly(ε-caprolactone). It was found that it was impossible to seal chitosan with a standard heat-pulse sealing technique. The whey-protein-isolate was sealable but the strength of the seals was lower than the intrinsic strength of the pure whey-protein-isolate. The folding endurance properties of chitosan and its blends were far better than those of the whey-protein-isolate and its blends.

Keywords: Poly(ε-caprolactone); Chitosan; Whey; Physical properties; Optical properties; Blends

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INTRODUCTION

Polymers that are a part of the natural ecocycle are very interesting as alternatives to petroleum-based polymers in many different applications. Concerns for the environment and the limited source of petroleum increase the interest in "native" polymers. Native or biodegradable polymers which have already found commercial use include polylactide, poly(hydroxy butyrate-co-valerate) and polyglycolide [1]. However, there is a debate as to whether the use of these polymers lowers the environmental impact, due to the high costs/energy involved in the purification and isolation of these polymers [1]. Future life-cycle analysis (LCA) will hopefully show whether these polymers actually have a higher impact on the environment than *e.g.*, polyethylene. From an environmental point of view, it may be better to use polyethylene and simply incinerate the polymer after use.

Whey protein and chitosan are two native polymers that belong to a special group of polymers obtained from "biological waste", and they may thus be treated differently in the LCA analysis [2–13]. Whey is a by-product from cheese-making and large quantities of this by-product are used for animal-feed, infant formulas and sport foods or are simply disposed of as waste [4]. Dairy companies are interested in finding alternative uses for this material. It has been shown that whey or specifically the whey proteins have good film-forming properties. Whey taken directly from cheese-making contains approximately 10% of the major whey protein constituent, but with subsequent purification the whey protein content, and hence the film-forming properties, can be increased to almost 100%. From a commercial point of view, however, it is interesting to use whey with as little whey protein as possible, since purification is expensive. The whey protein is brittle and acceptable film properties are therefore achieved only after the addition of a plasticiser *e.g.*, sorbitol or glycerol [14]. The plasticised polymer is relatively tough but its strength and stiffness are low [4].

Chitosan is obtained by partial or complete deacetylation of chitin that is the major component in shells of crustacians including crab, shrimp, krill, clam/oyster and squid [15]. It is also available from fungi [15]. Chitin is available as a waste product from the seafood processing industry. Chitosan resembles PETP in its properties. It is strong, tough and stiff and it has good optical properties [16].

There is an interest in exploiting these materials for packaging purposes. The commercial interest in packing milk in whey and packing shrimps in chitosan is obvious. There is however a major drawback in using these polymers as *e.g.*, packaging materials, in that they are very humidity-sensitive which limits their applicability in direct contact with foodstuff and also when they are exposed to human tissue [8, 17].

The purpose of this work has therefore been to reduce the humidity and water-sensitivity by adding poly(ε-caprolactone) to whey and chitosan.

Poly(ε-caprolactone) is one of the most hydrophobic polyesters existing today and, even though it is petroleum-based, it is biodegradable.

EXPERIMENTAL

Materials

A whey protein isolate, WPI, Lacprodan DI-9224, was supplied by MD Foods Ingredients (Denmark). Chitosan of medium molecular weight ($\overline{M}_w = 400\,000$ g/mol) was provided by Fluka Biochemika (Sweden). Glycerol and chloroform, trichloromethane stabilised with 1% ethanol, were purchased from Lab-Scan (Sweden). Poly(ε-caprolactone), PCL, TONE P-300 ($\overline{M}_w = 10\,000$ g/mol and $\overline{M}_w/\overline{M}_n = 1.7$), was supplied as granules from Union Carbide. Acetic acid glacial 100% was purchased from MERCK.

Sample Preparation

Chitosan-Films

To protonate the molecule $NH_2 \rightarrow NH_3^+$, to make it soluble in water, acetic acid was used. The most efficient way of preparing a chitosan solution was by first dissolving chitosan (1% w/w) in water during high-speed stirring and then adding acetic acid (1%) to the solution while stirring. Stirring was continued for 30 minutes until all the chitosan had dissolved. To ensure a homogeneous solution, it was mixed in a blender for 4 minutes. The solution was kept unstirred for 2 hours before it was decanted into petri dishes covered by Teflon-coated aluminium (Bytac from Norton Performance Plastics Corp.). Approximately 20 g of solution was poured into each petri dish. Films were dried for 48 hours at room temperature.

WPI-Films

An aqueous solution of 12% whey (w/w) and 6% (w/w) glycerol was stirred for 15 minutes at room temperature. In order to denature the protein, the solution was kept at 73°C for 20 minutes. It was then decanted into petri dishes covered by Teflon-coated aluminium (20 g in each) and subsequently dried for 48 hours at room temperature.

PCL /Chitosan-Films

An aqueous solution containing 1% chitosan and 1% acetic acid and a chloroform solution containing 10% PCL (w/w) were each decanted into separate glass tubes. Both solutions were mixed with a magnetic stirrer for 20 minutes. The chitosan solution was then mixed in a blender for 4 minutes and subsequently the PCL solution was added to the chitosan solution and the new solution was mixed for another 4 minutes. The solution was left to cool for 30 minutes and it was then dried in a vacuum oven for 10 minutes before it was decanted into petri dishes covered by Teflon-coated aluminium

(20 g solution was decanted in each dish). Vacuum drying removed air which was dissolved in the solution. Films were subsequently obtained after the solution had dried for 24 hours at 23°C and 30% relative humidity. Blends were prepared with 5, 10 and 15% by weight of PCL with respect to the chitosan added.

PCL/WPI-Films

The WPI and the PCL solutions were made as described above. The solutions were separately stirred until homogeneous solutions were obtained and they were then mixed together in a blender for 4 minutes. The obtained solution was cooled to room temperature. Subsequently, a foam layer was removed from the surface of the solution and the solution was then heated to 60°C for 20 minutes. After the second cooling to room temperature, the solution was allowed to dry in a vacuum oven for 10 minutes before it was decanted into petri dishes covered by Teflon-coated aluminium (25 g solution in each dish). Blends were prepared with 5, 10 and 15% by weight of PCL with respect to the WPI added.

Methods

Transparency

The transparency of the films was assessed by measuring the distance (L) between the specimen (polymer film) and a letter printed with black ink, with a line thickness of 300 μm, on a white paper at which the letter became invisible when viewed through the specimen. The distance between the polymer film and the observer was 40 cm.

UV/VIS-Spectroscopy

A Hewlett-Packard 8415A Diode Array spectrometer was used to measure the light absorption.

Printability

A red ethanol-based dye was applied as a single straight line on the surface. After intervals of 2 s and 30 s, a dried poly(methyl methacrylate) plate was drawn over the dye line to smear the line out. The distance of the smearing was measured. The shape and amount of dye left on the dye line after this "draw-down" procedure were analyzed qualitatively.

Scanning Electron Microscopy

Scanning electron microscopy was performed on specimens cracked at the temperature of liquid nitrogen or after Instron tensile tests at 23 ± 2°C. The samples were coated with gold/palladium before examination in the JEOL JSM-5400 scanning electron microscope.

Tensile Test

The stress-strain properties were obtained at 23°C (50% relative humidity) according to SCAN-P 38 : 80 (34) using an Alwetron TCT 10 tensile tester. Three samples of length 50 mm and width 15 mm were tested for each blend. The thickness of each specimen was taken as the average of five readings. The strain rate was 100 mm/min and the strain was measured as the separation of the clamps. The clamped length was 30 mm.

Seal Strength Measurements

Films (thickness = 0.1 – 0.3 mm) were welded in a Multivac A300 during 10 consecutive 0.2 s heat pulses. The seal strength of the welded films was determined in an Alwetron TCT10 tensile tester at 23 ± 2°C (50% relative humidity) and 100 mm/min strain rate. The clamped length of the specimen was 40 mm.

Flexural Stiffness

The stiffness of the blends was obtained by the standard test according to SCAN-P 29 : 95 using a Lorentzen and Wettre stiffness tester. The force to bend the specimen through an angle of 7.5° was monitored. The specimens had the dimensions 55 mm × 40 mm (clamp width) and the distance between the clamp and the point where the force was applied was 10 mm. The samples were conditioned at 23°C and 50% RH for 3 h before the measurements. The stiffness index (Nm^2/g) was obtained from the force (F) and the density (w) of the specimen: $S_i = F/w^3$. The stiffness index was calculated as the average of 3 – 4 specimens.

Folding Endurance Test

The folding test was performed according to SCAN-P 17 : 77 using a Lorentzen and Wettre folding endurance tester. Specimens preconditioned at 23°C for 24 h at 50% relative humidity (chitosan blends) and 25% relative humidity (WPI blends) were subjected to cyclic folding through ± 180° until fracture occured. Specimens were fixed in vibrating clamps at one end and the vibrational amplitude caused an imposed folding of the specimen. The 10-logarithm of the number of cycles until fracture ($\log(N_f)$) was calculated and averaged over 5 samples.

RESULTS AND DISCUSSION

Transparency is often a desired property for a food or medical packaging material. Figure 1 shows that the optical clarity of chitosan was higher than that of WPI. WPI contained globular particles and a "wavy" surface that decreased the optical clarity. The optical clarity of the chitosan blends was

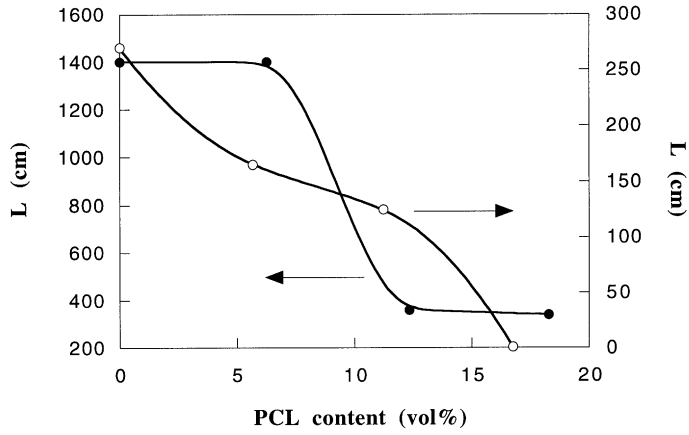

FIGURE 1 Transparency of PCL/chitosan blends (●) and PCL/WPI blends (○) as measured by the distance (cm) at which an object becomes invisible when viewed through the film. Note that the thickness of the chitosan blends ranges between 0.012 and 0.023 and the thickness of the WPI blends between 0.19 and 0.27 mm.

not affected below 5% PCL. Above 5%, the transparency decreased and the blends became opaque. However, transparency was still acceptable even for the films with 15 wt% PCL. The uniform color suggested a homogeneous dispersion of the PCL phase. The transparency gradually decreased with increasing PCL content also in the case of the WPI specimens and here the samples turned from beige to white and here too the homogeneous color suggested that the PCL was uniformly distributed in the blends. UV-VIS spectroscopy revealed that light transmission was high between 220 nm and 1100 nm for pure chitosan and between 320 and 1100 nm for pure WPI.

Printing the red dye on pure chitosan and on pure WPI yielded a solid thick line. The red dye was absorbed more rapidly in WPI than in chitosan and the general quality of the print was better on WPI. Figure 2 shows that the printability of chitosan, as measured by the smearing distance of the dye, was partly lost with increasing PCL content. The impact of PCL on the printability of WPI was negligible. These results therefore suggest that PCL was not present in the surface of the WPI blends. For comparison it should be mentioned that plain paper has a negligible smearing distance and that low-density polyethylene has a smearing distance of approximately 8 mm. On a moisturized chitosan surface, the smearing distance increased and the red dye line was thin.

The water-sensitivity and humidity-sensitivity of pure chitosan and of pure WPI are illustrated in Figures 3 and 4, which show the modulus and strain at break. The chitosan specimen exposed to liquid water had a 97%

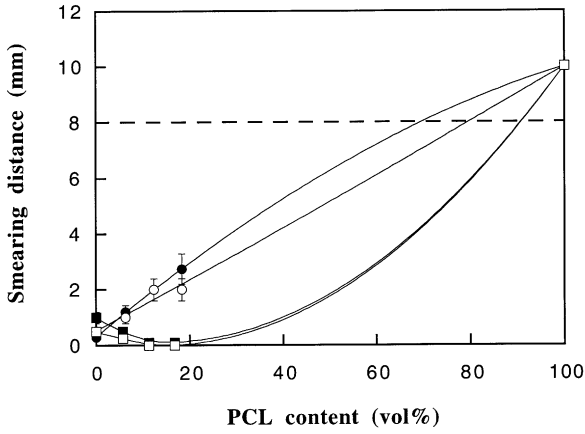

FIGURE 2 Red dye smearing distance 2 s (chitosan (•) and WPI (■)) and 30 s (chitosan (○) and WPI (□)) after being applied. The beam line indicates smearing distance for low density polyethylene.

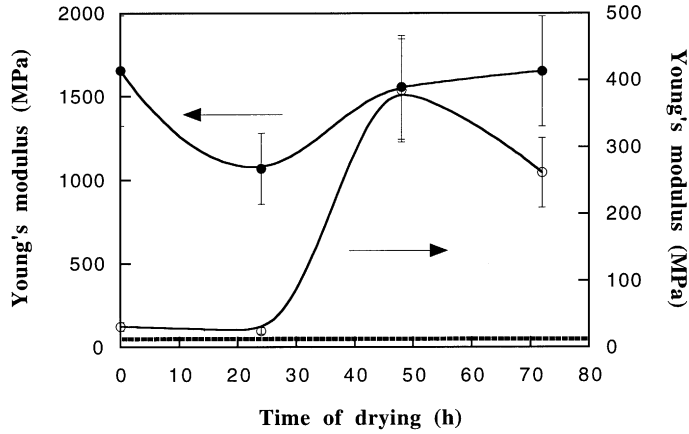

FIGURE 3 Young's modulus for chitosan (•) and WPI (○) as a function of drying time. The dotted line indicates the values for pre-wetted chitosan and WPI respectively.

lower modulus and a 69% higher fracture strain than the unexposed specimen. The corresponding values for WPI were 69% and 37% respectively. In order to reveal the effect of drying on the mechanical properties, the films were vacuum-dried at ambient temperature before the tensile tests. The impact of drying was high for WPI where the modulus

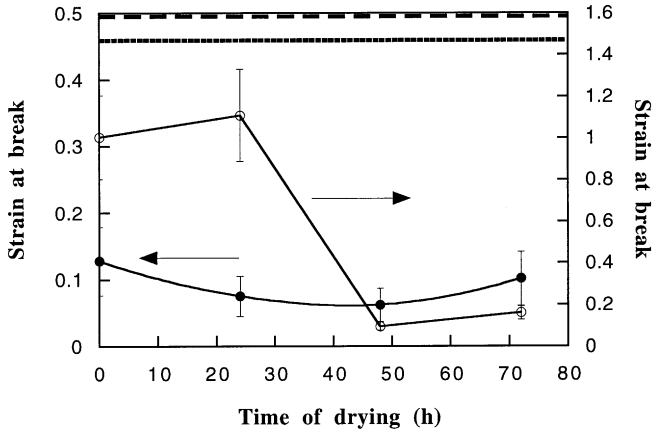

FIGURE 4 Strain at break for chitosan (•) and WPI (○) as a function of drying time. The dotted and dashed lines indicate the values for pre-wetted chitosan and WPI specimens respectively.

increased and the strain at break decreased with drying time. Interestingly, drying had no impact on the mechanical properties of chitosan. It is believed that the bound water in chitosan was not removed by the vacuum drying [18]. Yield stress and fracture stress followed the trends exhibited by the other mechanical properties and they are therefore not shown here. They decreased dramatically upon wetting and they also increased with drying time for WPI and remained more or less constant with drying time for chitosan.

The incorporation of PCL led to a rapid decrease in stiffness for chitosan and a relatively slow increase in stiffness for WPI (Fig. 5). The data lay within the series-parallel upper and lower boundary estimates and were adequately predicted by the Halpin-Tsai relationships [19]:

$$E = E_c \frac{1 + \zeta\eta\phi}{1 - \eta\phi} \tag{1}$$

$$\eta = ((E_d/E_c) - 1)/((E_d/E_c) + \zeta) \tag{2}$$

where $\zeta = 3^{0.5} \log(w/l)$, and where w and l are respectively the width and thickness of the dispersed component, ϕ and E_d are respectively the volume fraction and modulus of the dispersed component and E_c is the modulus of the continuous component. Best fit of the PCL/chitosan data yielded an average width-to-thickness ratio of 1.5 for the dispersed PCL phase. This is in agreement with the SEM-data shown in Figure 6a. The width-to-thickness ratio of the PCL domains in PCL/WPI were found to be

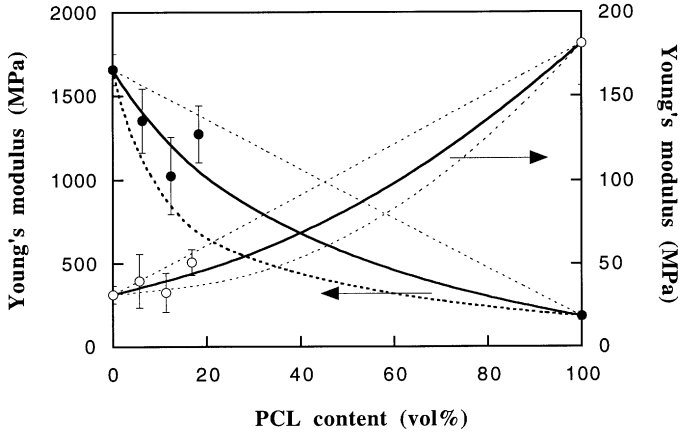

FIGURE 5 Modulus for PCL/chitosan blends (●) and PCL/WPI blends (○). Solid lines represent best fits of the Haplin Tsai-model with a width-to-thickness ratio of 1.5 (PCL/chitosan) and 50 (PCL/WPI) and dashed lines are upper and lower boundary estimates.

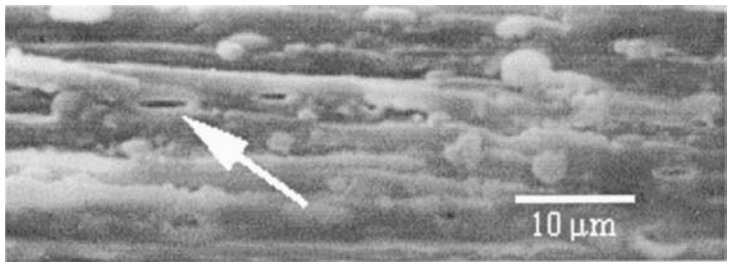

FIGURE 6a Scanning electron micrograph of PCL/Chitosan (15/85). Arrow shows a hole left from an elongated PCL-particle.

approximately 50. This value seems to be rather high, but this may be explained by the fact that the PCL domains are fibrous (Fig. 6b). The Halpin-Tsai model predicts a value of unity for ζ, clearly inconsistent with the moduli data. Lewis and Nielsen [20] modified the Halpin-Tsai model and using their model it was possible to obtain a perfect fit for PCL/WPI as shown in Figure 5. The modified model yielded a fiber length-to-diameter ratio of 4–6.

The fracture stress decreased linearly with increasing PCL content in the PCL/chitosan blends and the specimens always showed yielding before fracture (Fig. 7). This was also confirmed by the strain values that decreased only mildly with increasing PCL content (Fig. 8). It seems that the adhesion

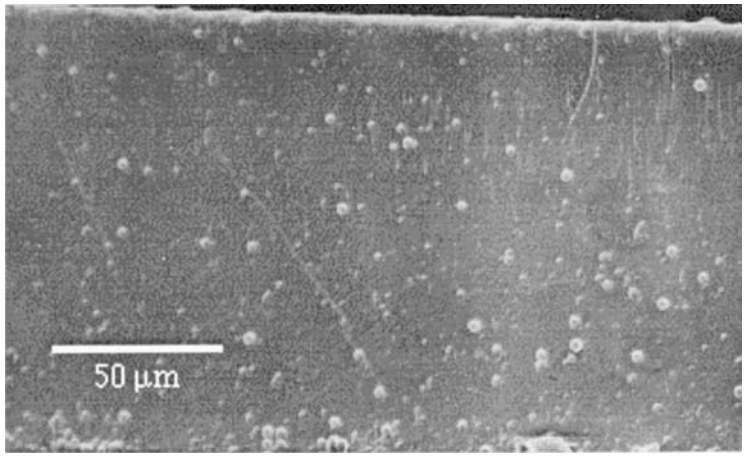

FIGURE 6b Scanning electron micrograph of PCL/WPI (5/95).

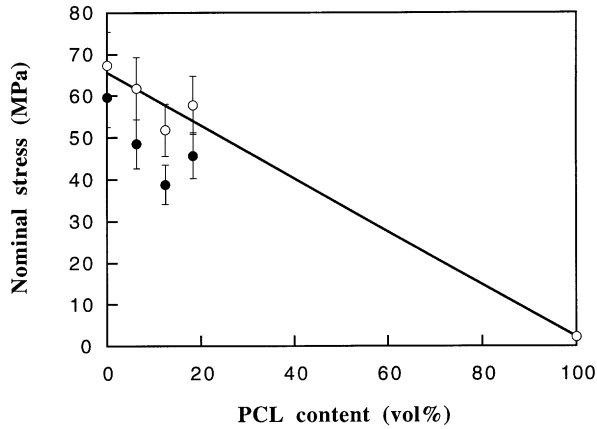

FIGURE 7 Yield stress (●) and fracture stress (○) for PCL/chitosan blends. The line is drawn to show the linearity.

was good between the two components, which was also the conclusion drawn from density data [21].

The fracture stress was low for both WPI and PCL (Fig. 9). The absence of any large decrease in fracture stress at intermediate PCL contents and the presence of a yield stress showed that the toughness of WPI was not greatly altered by the addition of PCL. The fracture strain decreased with increasing PCL content, but the yield strain remained constant. Hence all blends were considered tough even though toughness decreased as a result of the addition of PCL (Fig. 10).

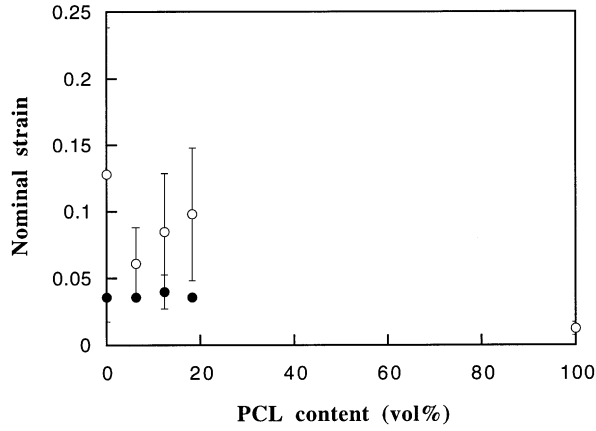

FIGURE 8 Yield strain (●) and fracture strain (○) for PCL/chitosan blends.

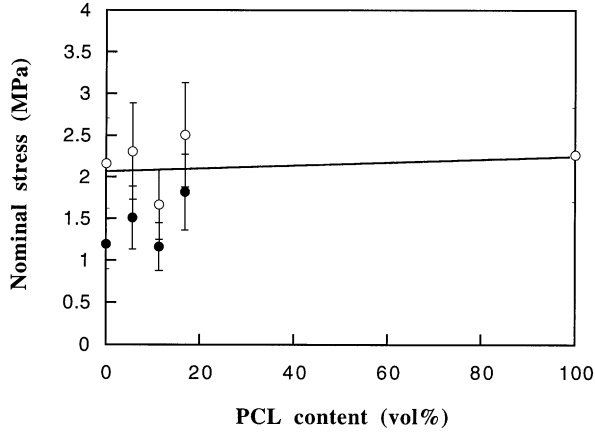

FIGURE 9 Yield stress (●) and fracture stress (○) for PCL/WPI blends.

Sealability or retortability is an important property of packaging materials. It was found that it was impossible to seal chitosan and its PCL blends with the standard sealability equipment used. This was not surprising, since the material resembles PETP that is also difficult to seal. Sealing of chitosan thus requires alternative techniques. WPI and the WPI blends were readily sealable, but the seal strength was lower than the intrinsic material strength (Fig. 11). The seal strength of the PCL/WPI blends decreased with increasing PCL content. Fractures were brittle and occurred at the seal lines.

For packaging materials, it is essential to know the bending stiffness of the material *via* the stiffness index. It is also essential to know the resistance

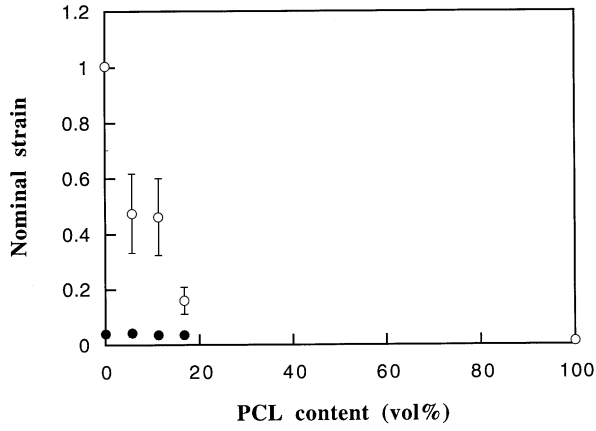

FIGURE 10 Yield strain (•) and fracture strain (○) for PCL/WPI blends.

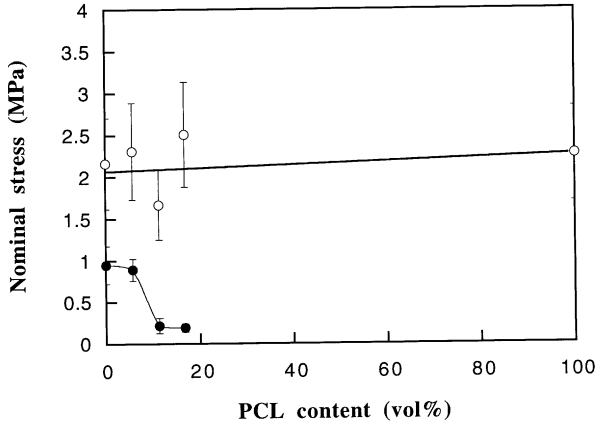

FIGURE 11 Fracture stress (seal strength) of the sealed (•) and unsealed (○) specimens.

to fracture if the material is subjected to repeated folding. Figures 12 and 13 show the stiffness index and the logarithm of the number of folds until fracture for PCL/chitosan and PCL/WPI blends. Data for pure PCL is absent because the grade used here was extremely brittle at low thicknesses, and this made it impossible to evaluate it in these tests. In accordance with the above modulus data, the stiffness calculated from the bending test (stiffness index) was much higher for chitosan than for WPI. Interestingly, the resistance to repeated folding was much lower for WPI than for

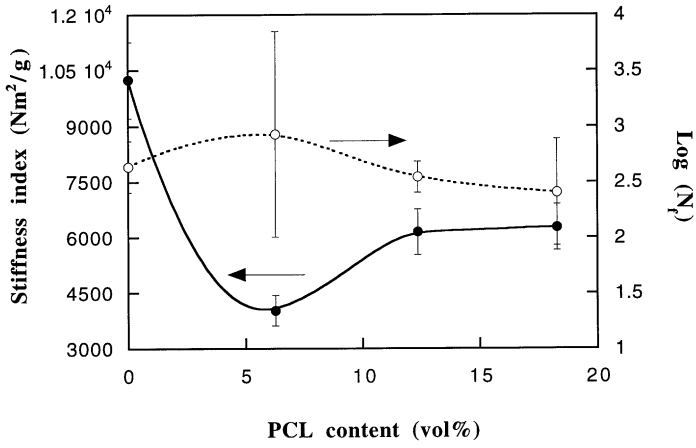

FIGURE 12 Stiffness index (●) and number of double folds until fracture, log(N_f), (○) as a function of PCL content in chitosan.

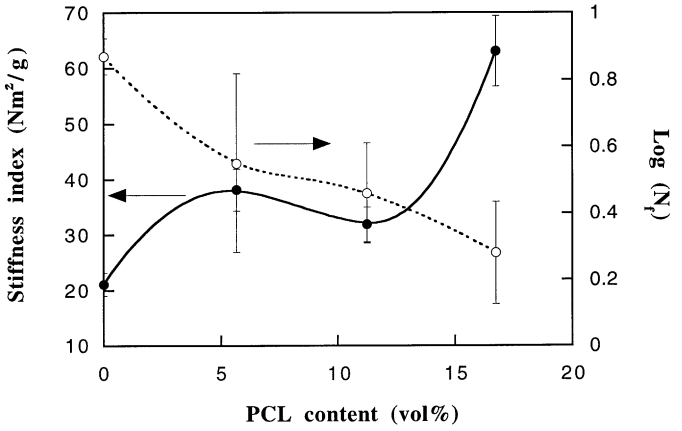

FIGURE 13 Stiffness index (●) and number of double folds until fracture, log(N_f), (○) as a function of PCL content in WPI.

chitosan, whereas the strain data (Figs. 8 and 10) showed that WPI was the tougher material. It seems that the fatigue properties of WPI, which are measured indirectly through the folding test, were inferior to those of chitosan. The addition of PCL to chitosan reduced the bending stiffness, as is expected from the tensile modulus data. Nevertheless, log(N_f) was not lowered, which is very promising for future packaging applications. The

effects of adding PCL to WPI were different. In agreement with data for modulus and fracture strain presented earlier, the bending stiffness increased and $\log(N_f)$ decreased with the addition of PCL.

CONCLUSIONS

Transparency and printability were not severely altered by the addition of PCL. WPI had better printability properties and printability was not greatly altered by the addition of PCL. Liquid water had a dramatic effect on the stiffness and the toughness of both chitosan and WPI. All blends were relatively tough but the stiffness depended on the content of PCL. The change in modulus followed the Halpin-Tsai model. Chitosan was difficult to seal whereas WPI was sealable. The strength of the seals of WPI and its blends was however lower than the intrinsic strength of the corresponding materials. In the case of chitosan, the folding endurance was not altered by the addition of PCL, but in the case of WPI it decreased with the addition of PCL.

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