

Effect of Starch Predrying on the Mechanical Properties of Starch/Poly(ϵ -caprolactone) Composites

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ABSTRACT: This study describes the effect of predrying sago starch, a tropical starch, on the resultant mechanical properties of starch/poly(ϵ -caprolactone) composite materials. Sago starch was dried to less than a 1% moisture level in a vacuum oven and dispersed into a polycaprolactone matrix with an internal mixer at 90°C. The mechanical properties of the composite were studied according to methods of the Association for Standards, Testing, and Measurement, whereas the morphology was monitored with scanning electron microscopy. The properties were compared with a composite obtained with native starch containing 12% moisture. The results indicated that predrying the starch led to a lower property drop rate in the composite as the starch content

increased. The elastic modulus, tensile strength, and elongation at break were higher than those obtained when starch was used without predrying. The morphology observed during scanning electron microscopy studies was used to explain the observed trends in the mechanical properties. In this way, a relatively simple and cost-effective method was devised to increase the starch loading in the polycaprolactone matrix to obtain properties within the useful range of mechanical properties. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 877–884, 2003

Key words: composites; mechanical properties; biodegradable

INTRODUCTION

In the ongoing quest for the most suitable, cost-saving processing conditions for the production of biodegradable materials such as starch/polycaprolactone (PCL) composites, the predrying of starch before incorporation into the matrix seems to have received little attention. Predrying was used previously by Griffin¹ for a starch/polyethylene system. Earlier work on the incorporation of starch into PCL involved its use as obtained, that is, with moisture levels ranging from 10 to 14%^{2,3} and without any form of pretreatment. Other methods include various modifications, which could be divided into those methods leaving the granular structure intact, such as crosslinking with epichlorohydrin⁴ or mixed anhydrides⁵ and phosphate crosslinking,⁶ with a concomitant granule size reduction, and those completely destructuring the granule. The former materials involving modified starch have the advantages of stability under humidity and temperature fluctuations,^{7,8} whereas the degradability can be controlled by variations in the extent of modification.⁹ Other attempts include the for-

mation of semipenetrating and interpenetrating networks, in which destructured starch and PCL are interlinked with the hope of increasing the melting temperature and slowing the biodegradation rate.¹⁰ The major disadvantage of these techniques is the increased cost of the starch due to its modification. A justification for the modification cost can, however, be achieved only when the desired effects are achieved. The most promising method of starch incorporation is its use in its extended form (thermoplastic or destructured) with an array of plasticizers, such as glycerol,¹¹ propylene glycol,¹² and poly(vinyl alcohol).^{13,14} This affords the opportunity of an increased starch loading, relative to the granular starch,¹⁵ even after the weight percentage of the added plasticizer is discounted. Fritz et al.¹⁶ incorporated thermoplastic starch into a PCL matrix up to a 60 : 40 ratio. They reported that a closely meshed two-phase structure developed, and the measured mechanical properties were within the useful range. However, the resulting material was less stable because of plasticizer migration, which ultimately led to embrittlement and the loss of properties. Moreover, two or more processing steps were involved. Unlike other thermoplastic matrices, such as polyethylene and polypropylene, PCL tends to accommodate a larger amount of particulate fillers. Granular starch contains moisture, and it has been widely reported that this moisture escapes during extrusion and blending^{17,18} because most of the water present within starch granules is interstitial, and so when the

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TABLE I
Tensile Properties of Pre-dried and Native Sago Starch/PCL Composites

Starch content (w/w)	Tensile strength (MPa)		Elongation at break (%)		Yield strength (MPa)		Modulus of elasticity (MPa)	
	<i>Predried</i>	<i>Native</i>	<i>Predried</i>	<i>Native</i>	<i>Predried</i>	<i>Native</i>	<i>Predried</i>	<i>Native</i>
	0	44.01 ± 2.4	44.01 ± 2.4	902.67 ± 72.12	902.67 ± 72.12	14.89 ± 0.34	14.89 ± 0.34	288
10	37.99 ± 0.65	34.44 ± 1.89	885 ± 23.65	825.33 ± 32.12	13.06 ± 0.26	12.85 ± 0.24	329	315
20	29.49 ± 2.7	25.47 ± 1.7	721.16 ± 23.39	670.33 ± 30.1	10.74 ± 0.54	10.71 ± 0.34	399	367
30	26.73 ± 0.76	22.27 ± 1.73	693.33 ± 38.95	575.17 ± 25.19	9.47 ± 0.35	9.24 ± 0.4	440	407
40	22.35 ± 0.53	19.57 ± 1.19	624.33 ± 33.98	553.17 ± 29.29	8.99 ± 0.29	9.06 ± 0.23	500	479
50	12.21 ± 1.68	12.06 ± 1.30	464.5 ± 51.46	435.16 ± 36.66	7.53 ± 0.44	7.25 ± 0.96	558	548

temperature approaches 100°C (the boiling point of water), it vaporizes. PCL is, however, hydrophobic, and the inclusion of moisture in the matrix could result in some degree of instability. This effort is directed at reducing the overall cost of biodegradable PCL-based materials suitable for food packing and food service applications. The approach here involves the predrying of starch, a technique that does not require major equipment modification or added cost. Predrying before processing is a normal process for plastics, such as nylon, polycarbonate, and most engineering plastics. The effects of the exclusion of water molecules from the composite were examined according to the stress-strain relationship under load and the morphology, and they were compared with the results for when starch was used as obtained.

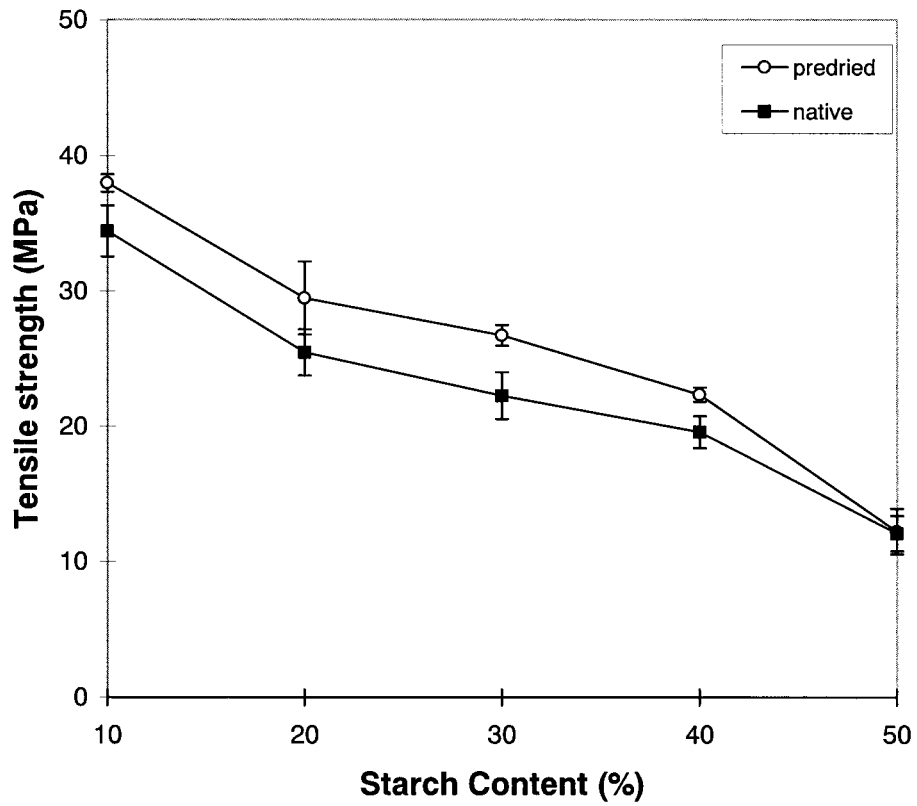
EXPERIMENTAL

Poly(ϵ -caprolactone) (weight-average molecular weight = 80,000 g/mol; Tone P-787) was supplied by Union Carbide of Asia Pacific, Inc. (Singapore). Sago starch was obtained from Craun Research (Sarawak, Malaysia). The sago starch, as obtained, contained 12% moisture.²⁰ It was dried to a moisture content of less than 1% with a vacuum oven set at 70°C and 30 kPa for 72 h. The dried starch was stored over phosphorous pentoxide in a desiccator until it was required. Compounding was performed at 90°C and a rotor speed of 40 rpm with a Brabender PLE-331 plasticorder internal mixer equipped with a double mixing cam. PCL was charged into the mixing chamber and allowed to melt, and it was followed by the gradual addition of starch granules, with sufficient time allowed for the starch particles to be worked into the matrix. Mixing was allowed to continue for 20 min. Different ratios of starch/PCL composites were prepared to give mixing ratios of 0–50 wt % of starch dispersed in PCL in 10% increments. For comparison, starch with 12% moisture (native starch) was used as a control. Effective mixing was indicated by a stable torque-time curve, at which point stage blending was stopped. The blends were sheeted out onto a two-roll mill and then were compression-molded into sheets 1.0 mm thickness at 90°C and 10 MPa with a Kao

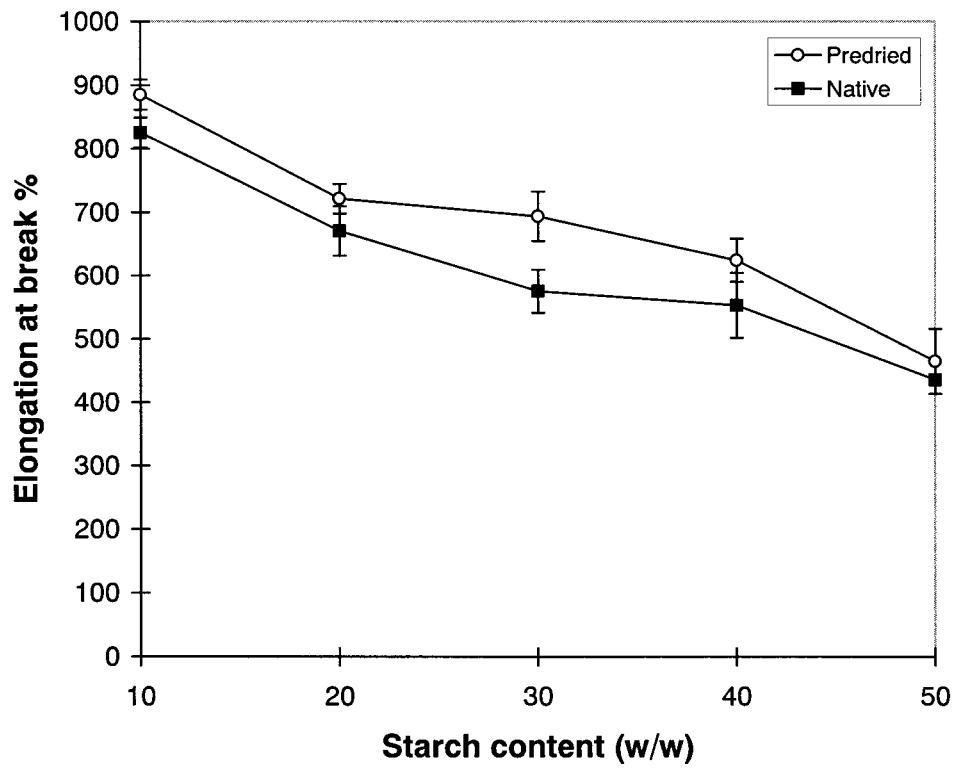
Tieh Gotech KT-7014A compression-molding machine. Dumbbell samples were cut from the prepared sheets according to Association for Standards, Testing, and Measurement (ASTM) specifications and were conditioned in desiccators containing phosphorous pentoxide and placed in the measuring room for 24 h at 20°C. The undried samples were conditioned at 60% relative humidity. The tensile tests were conducted according to ASTM Standard D412-68 with a Monsanto T10 tensometer. The initial grip distance was 50 mm, and the test speed was 30 mm/min. The results are an average of six determinations. Morphological studies were conducted with a Leica Cambridge S-360 scanning electron microscope. Scanning electron microscopy (SEM) studies included observations of the starch granule dispersion, which was critical for determining the effects of the increased volume fraction of starch; the mode of deformation of the PCL matrix phase; and the fracture surfaces. Attempts at measuring the particle sizes of starch as a result of drying were also observed.

RESULTS AND DISCUSSION

Table I and Figure 1 show the results of the mechanical properties of the matrix as a function of the starch loading. The effects of predrying the starch on the mechanical properties are also indicated. In general, the tensile strength, elongation at break, and yield stress decreased as the starch content increased. The modulus (a measure of stiffness), however, increased with increasing starch content in all cases. These trends agreed with previous work on the effects of rigid particulate fillers on the mechanical properties of thermoplastics.^{2,3,10,19,20} When starch granules are gradually introduced into a molten PCL matrix under shear, the particles are distributed uniformly within the matrix over time as long as the optimum rheological conditions are achieved. PCL has been reported to be a good dispersant of particulate materials.²¹ The uniform dispersion of particles is of the utmost importance in assessing the effects of particulate fillers on the overall properties of a composite. Sago starch is made up predominantly of ovoid granules containing 10–14% moisture. The starch gelatinizes at 72°C in the

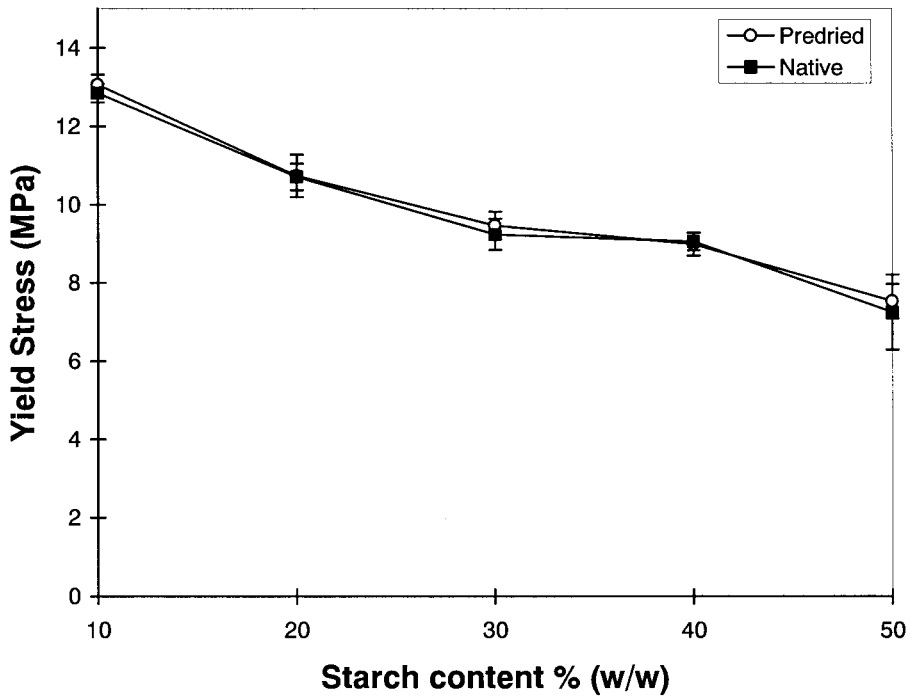


(a)

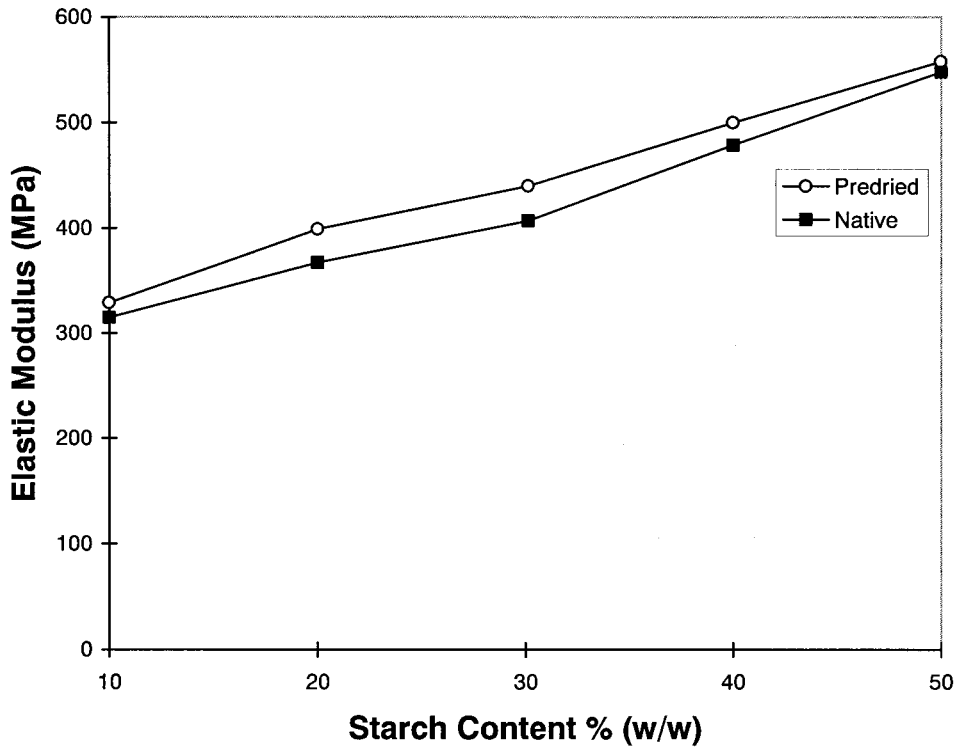


(b)

Figure 1 Comparative tensile properties of predried and native starch/PCL composites: (a) tensile strength, (b) elongation at break, (c) yield stress, and (d) Young's modulus. The individual properties are plotted as functions of the starch loading.



(c)



(d)

Figure 1 (Continued)

presence of adequate water (starch/water = 1 : 3). At low moisture contents (12% in this case), because of the low thermal conductivity of starch, there is a need for a very high shear and temperature before gelatinization can be achieved. When sago starch is, however,

dried to less than a 1% moisture content, the possibility of gelatinization is removed. For native starch, at 90°C (the temperature at which blending is carried out), the conditions of shear lead to a rise in the melt temperature, and some water molecules escape from

the granule. These may become trapped within the hydrophobic and water-repellent PCL matrix, whereas some escape from the composite entirely. The escapee water molecules trapped within the PCL matrix may become secondary fillers. These fillers, because of their high mobility, will lead to a higher degree of instability within the matrix because they will present as voids. These voids could serve as areas of stress concentration and, consequently, as centers of failed initiation under tensile stress.

There is a significant difference ($p < 0.05$) in the values of the tensile strength, elongation at break, and modulus up to a 40% starch loading between the composites containing predried starch and native (moisture-containing) starch. At a 50% loading, however, the differences are no longer significant ($p < 0.05$). The apparently higher property retention for predried starch could be due to decreased interfacial tension between the matrix and the starch as a result of water exclusion leading to increased adhesion between the PCL and starch. Moreover, the predrying process is believed to be accompanied by a reduction in granule sizes of the sago starch, which leads to an increased surface area of contact between starch granules and PCL. Smaller particles are generally regarded as more reinforcing when used as fillers for thermoplastics. At a 50% starch loading, there was no discernible difference in the properties when starch was predried. A very recent observation is that sago starch contains polyphenols (0.8 mg/g). These phenolics could act as coupling agents between starch and PCL. This laboratory is investigating the possible role of phenolics in composites.

Yielding in PCL initiates by shearing [Fig. 2(a)]. Under this mechanism, the molecules slide or slip over one another when subjected to steady dynamic stress. Most polymers respond to such external stresses by some form of molecular rearrangement,²⁵ called *relaxations*, which tend to dissipate such imposed stresses. The stress-strain curves for PCL containing 0, 20, and 50% starch, shown in Figure 3, indicate that PCL undergoes a viscoelastic response typical of thermoplastics. However, a smooth curve was not obtained for PCL. There was a relaxation/recovery profile indicated by a slight drop in the internal stress during deformation. This (wobbly profile) was strain-rate-dependent because it was absent at a low machine speed (10 mm/min), which is indicated by the dotted line in Figure 3. Furthermore, at starch contents of 20% and greater, the relaxation/recovery profile is no longer observable on the stress-strain curves. At this point [Fig. 2(b)], the mode of deformation apparently changes, as the initial deformation, which initiates at a 45° angle to the tensile axis [Fig. 2(a)], is replaced by stress whitening (or crazing) occurring over the entire gauge length. It is suggested that this change in the mode of deformation could be due to the creation of

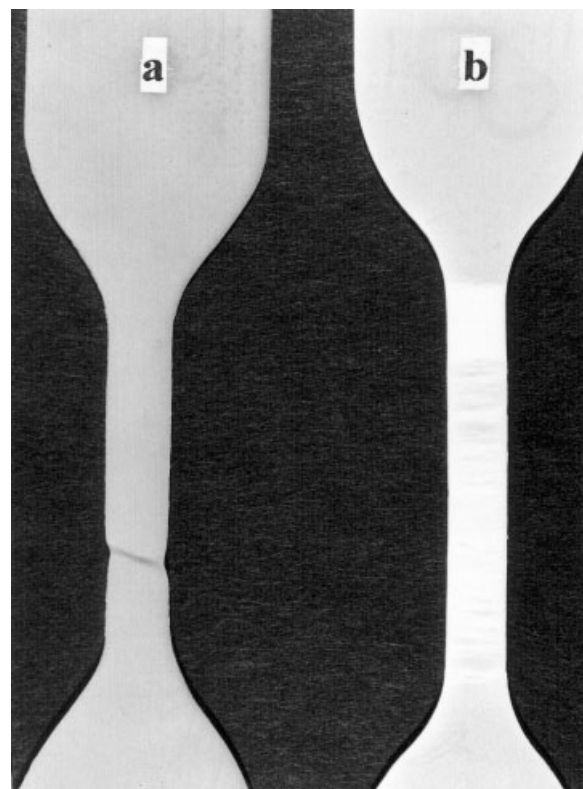


Figure 2 Images showing the yielding of PCL and a starch/PCL composite (20/80): (a) the yielding of PCL initiating at a 45° angle to the tensile axis and (b) stress whitening occurring over the entire gauge length of the specimen.

voids (seen in the SEM images of the tear fracture surfaces) interfering with the shear mode of deformation. Also, the introduction of particulate fillers into a matrix such as PCL contracts the area available for matrix materials to respond to the effect of deformation.²² Therefore, a different mode of deformation becomes apparent at starch loadings of 20% and greater. However, at a 50% starch content, the difference between predried starch and native starch becomes less significant because of filler-filler interactions. Regarding the yield point [Fig. 1(c)], there is no significant difference ($p < 0.05$) between drying and not drying, although the predried starch showed higher yields in most cases. This is attributable to the mechanism of yielding, which does not distinguish between the filler sizes once a particular filler ratio is achieved. The voids created, originating from the interface between the starch and PCL, seem to be of more importance. It is suggested that because of the broad particle size difference for sago starch (10–50 μm , mean = 35 μm), the effect of the particle size reduction as a result of drying, which shows prominently in the elongation at break and tensile strength, is not significant in the initiation of yielding. A steady decline in the yield point is observed in all cases.

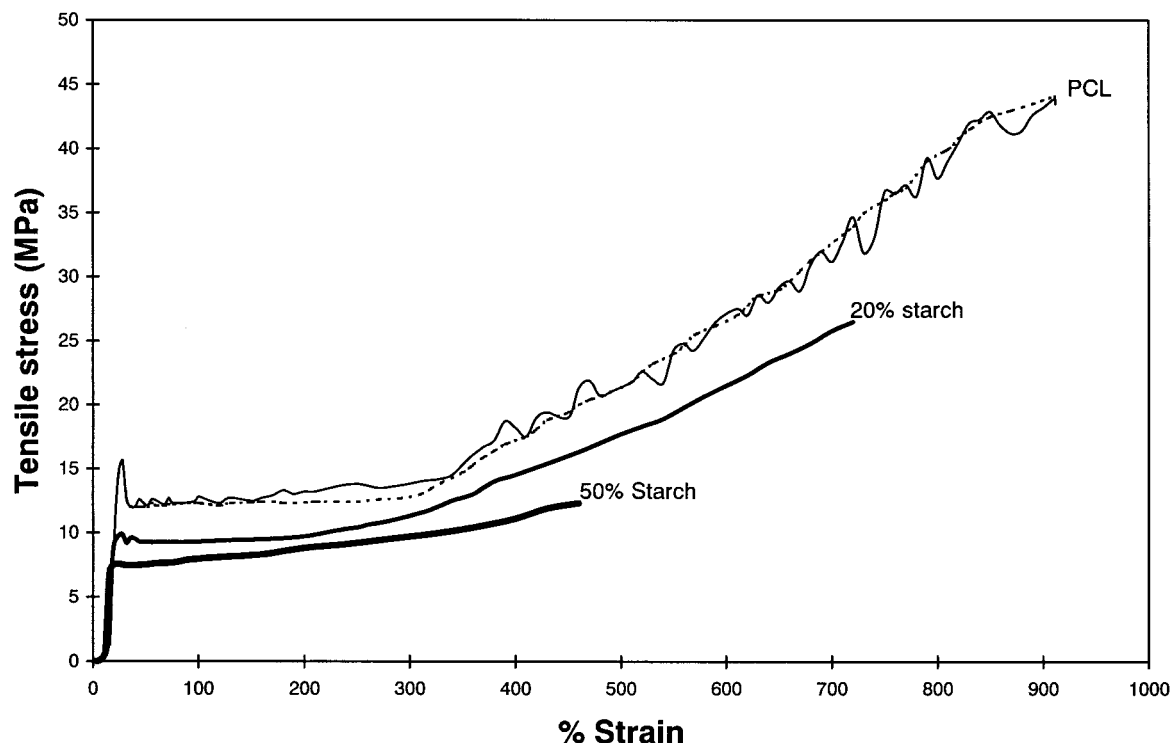


Figure 3 Stress–strain curves for PCL and for PCL/20% starch and PCL/50% starch composites at a 30 mm/min strain rate. The dotted line shows the difference at a 10 mm/min strain rate. The profile shows a strain relaxation/recovery for PCL alone, whereas the recovery profile was absent for the 20 and 50% starch loadings.

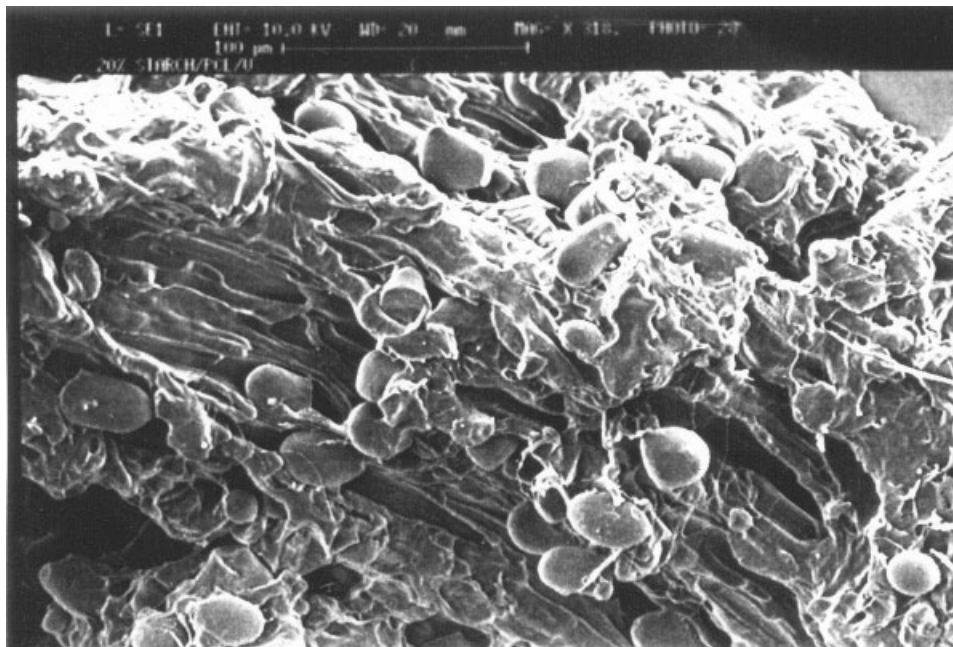
The modulus was derived from the elastic region of the stress–strain curves. As expected, the moduli of the composites increased with the increasing amounts of starch incorporated. This trend is expected when high-modulus fillers are used, even for situations in which reinforcement does not occur.^{19,22,24} The predried starch composite showed higher modulus values than the native starch composite, probably because of the reduced particle size effect and reduced interfacial tension. The higher increases in modulus at a 20% starch loading in all cases coincide with the observed disappearance of the relaxation/recovery profile on the stress–strain curve.

Figure 4 shows the morphology of the composites derived from the fracture surfaces. It is obvious that PCL forms the continuous matrix phase, whereas sago starch is the dispersed phase. It was not possible to measure interfacial distances when sago starch was predried, as opposed to when native starch was used. The skin and core regions of the test pieces did not show any differences resulting from atmospheric water sorption. The swelling energy of starch was not expected to be enough to distort the rigid PCL matrix and show a skin–core difference. Figure 5 shows the voids created as a result of the imposition of dynamic stress on the composite. There was no chemical bonding between the components of the composite; that is, there were

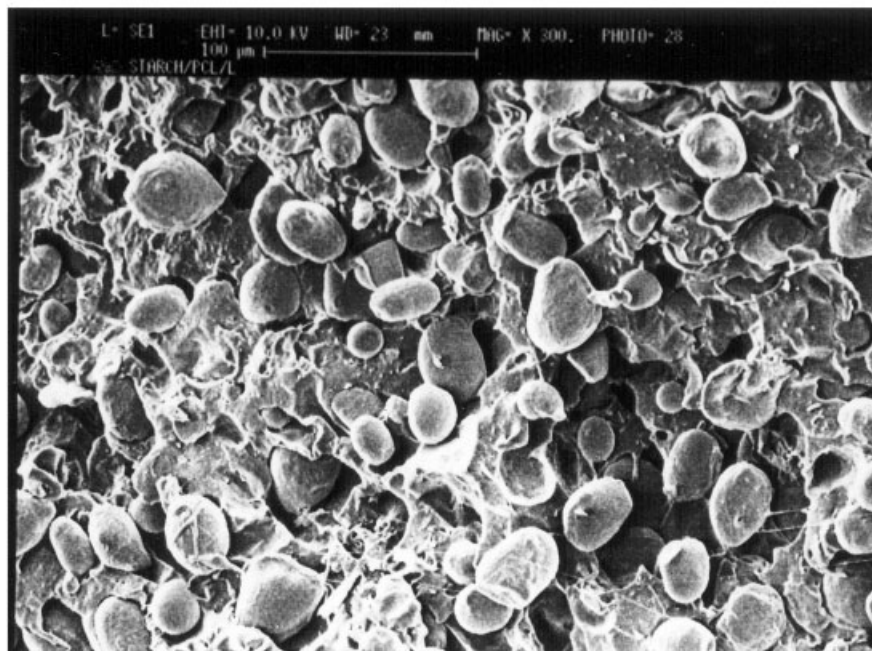
interfaces of different sizes. During dynamic deformation, the interface led to the generation of voids, which were not dependent on the original sizes of the interfaces. The voids were thought to interact with the shear bands and accelerate the yielding of the starch/PCL composites. It is believed that the sago starch particles interrupted the energy transfer within the matrix, creating voids (drawn along the tensile axis), as shown in Figure 5, which ultimately led to the nature of the failure and the yield observed in the composite.

CONCLUSIONS

The results of this investigation indicate that predrying starch to a moisture level of less than 1% leads to a general improvement in the properties of starch/PCL composites. There was a significant difference ($p < 0.05$) in the tensile strength, elongation at break, and modulus when starch was predried and when it was not before incorporation into a PCL matrix. The yield point, however, appears to be insignificantly affected, although the predried starch composites showed generally higher values. It is concluded that under the conditions with which native starch is incorporated into a PCL matrix, some water molecules escape the starch granules during processing and become secondary fillers,



(a)



(b)

Figure 4 SEM micrographs of the fracture surfaces of PCL and starch/PCL composites: (a) 20/80 and (b) 50/50 starch/PCL. The effect of an increasing starch loading on the composite morphology is seen. The predried composites alone are shown because there were no discernible differences from the native starch composites.

with pronounced effects on the mechanical properties of the composites. The yielding mechanism of PCL is also affected by the incorporation of starch. At starch contents of 20% and greater, the deformation mode changes from shear banding to crazing. A longitudinal section of the fracture surfaces reveals

voids drawn along the tensile axis. The predrying of starch could yield blends with better mechanical properties within the useful application range in comparison with other means of starch incorporation involving the presence of water, such as thermoplastic starch and native starch.

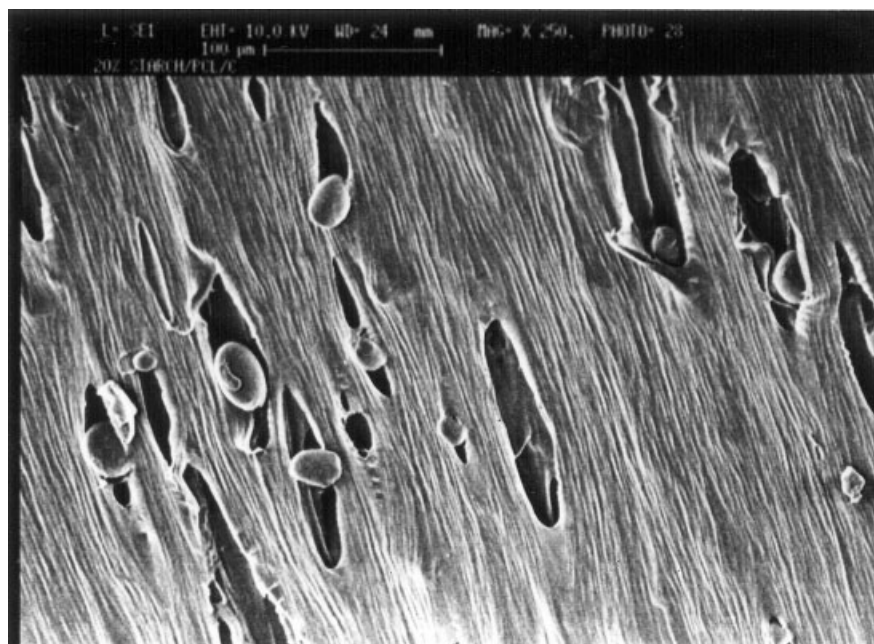


Figure 5 SEM micrograph of the longitudinal section through the fracture surface of a starch/PCL (20/80) composite. Voids originating from the interfaces between the components are evident after deformation.

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