

Properties of Extrusion Cast Sheets of Blends of Natural and Aliphatic Polyesters

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ABSTRACT: Natural and synthetic polymers of various compositions were blended in a twin-screw extruder. These blends were then sheeted into thin sheets with a coat hanger die attached to a single-screw extruder. The natural content in the blend was varied between 5 and 50 wt %, and the mechanical and morphological properties of the blends were evaluated. At 50 wt % natural content, the tensile strength decreased to a third of that of the synthetic polymer. The use of a compatibilizer doubled the tensile strength for the 50 wt % natural content blend. The sheets displayed equal strengths in the machine and transverse direction. The tear strength decreased as the natural content increased, and the decrease was greater in the anhydride-compatible blends than in the incompatible blends. The blends displayed two distinct glass transi-

tions, one for each component, indicating phase separation. The crystallinity of the blends decreased as the starch content increased. This result was confirmed by differential scanning calorimetry (DSC), which showed that the melting endotherm decreased as the starch content increased. Gel permeation chromatography (GPC) results showed that the peak position was at the same location irrespective of blend composition, indicating minimal degradation of starch moieties. The water absorption was diffusion controlled, with a sharp initial burst of water uptake. Scanning electron microscopy (SEM) showed melting of starch granules that formed a co-continuous phase with the synthetic polyester. Increasing the natural content also increased the surface roughness of the sheets. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1545–1554, 2003

INTRODUCTION

The vast majority of plastic products are made from nondegradable petroleum-based synthetic polymers. These products do not degrade in the landfill or in a compost-like environment. Thus, the disposal of these products poses a serious environmental problem.

A major source of pollutants is packaging films, tapes, and sheets that are mostly single use items. These items account for an estimated three billion pounds annually in the United States. Additional packaging concerns include thermoformed clamshells used in grocery stores and restaurants. It is difficult to cast films from purely agricultural materials. Attempts to solvent cast materials have shown limited success.^{1–6} When made from purely agricultural materials, such as gluten (wheat proteins) or casein (milk proteins), these films tend to display some serious drawbacks. The tensile strengths are often poor and, because these films contain a significant amount of plasticizer, their properties tend to change (the material stiffens) as the plasticizers diffuse out. Also, solvent disposal is often a costly process because of the strict environmental regulations.

An economical way of producing film or sheets is by flat film extrusion using chill-roll casting. In this process, the melt is plasticized and shaped into a planar structure, then cooled and stabilized when in contact with a roll before being wound up. The die takes the melt from the extruder, typically in a continuous rod shape, and spreads the melt into a wide sheet of uniform thickness. Films from poly(propylene) and polyamide are primarily produced in this manner. It would be difficult to produce a simple mixture of starch or proteins and plasticizers in this manner. The high viscosity of the melt along with the poor elongational properties and poor tear strength make it difficult to process.

One alternative is to blend agricultural materials with synthetic polymers that are biodegradable. Most aliphatic polyesters, such as polycaprolactone (PCL), poly(lactic acid) (PLA), and polyhydroxybutyrate-co-hydroxyvalerate (PHBV), are biodegradable. However, the cost of these materials is several (4–10) times that of the nonbiodegradable synthetic polymers they are designed to replace. Hence, based on economics alone, these biodegradable polyesters have not made any inroads except in some niche markets. Blending with cheap agricultural commodities, such as starch or proteins, has the potential to reduce the cost, provided acceptable physical and functional properties can be obtained.

New materials prepared by mixing natural and synthetic polymers result in products that display re-

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duced physical properties. Such polymers are thermodynamically immiscible, which precludes generating a truly homogeneous product because of high interfacial tension and poor adhesion between the two. The high interfacial tension, along with high viscosities, contribute to the inherent difficulty of imparting the desired degree of dispersion to random mixtures. This difficulty leads to their subsequent lack of stability and results in gross separation or stratification during later processing or use. Poor adhesion leads, in part, to very weak and brittle mechanical behavior.

Research has shown that as a consequence of the inherent immiscibility of biodegradable polyesters, only a relatively small amount of starch (<30% by weight) can be incorporated into the polyester. By modifying the polyester, it is possible to increase the miscibility and compatibility with starch or proteins so that the resultant blend properties may be synergistic and the morphology of the minor phase in the modified matrix polymer is finer and more homogeneous.

The objective of this study was to evaluate the physical, morphological, and the functional properties of films/sheets (>150 μm) made from blends of natural and synthetic polymers as a function of various process conditions and blend compositions. The natural polymers included both starches and proteins, and the biodegradable synthetic polyester was suitably modified to incorporate a functional group.

EXPERIMENTAL

Materials

Bionolle™ 1001, a poly(butylene succinate) copolymer [melt flow index (MFI), ~ 1.0] was obtained from Showa Highpolymer Company Ltd. (Tokyo, Japan). The number (M_n) and weight (M_w) average molecular weights of Bionolle 1001 are 83,650 and 205,580, respectively. The MFIs were determined by the ASTM test method D1238 at 190°C using a 2.16 kg load. These polyesters were incorporated with a maleic anhydride (MA) functional group using a procedure described elsewhere.⁷ Briefly, the anhydride was grafted onto the polyester by reactive extrusion in the presence of a free-radical initiator (dicumyl peroxide). Common wheat starch (70% amylopectin and 30% amylose) was blended with the polyester. Each blend also contained 5% wheat gluten, titanium dioxide (4 Fr), and optical brightener (0.01 Fr).

Blend preparation

The blends were prepared using a laboratory scale co-rotating twin-screw extruder (Rheomex TW-100, Haake Scientific Instruments, Paramus, NJ). The barrel length-to-diameter ratio was 20:1 and was divided

into four zones. The temperature in each zone could be controlled and adjusted to desired levels. The temperatures in the first four zones from the feed section during blend preparation were 120, 130, 130, and 120°C, respectively. The screw speed used was 60 rpm, which gave an approximate residence time of 40–45 s. A mixture of maleated polyester starch, gluten, and the required amount of respective unmodified polymer were introduced to the extruder with a vibratory feeder, and the resulting extrudate was chopped and ground to obtain samples for sheeting. The starch and gluten were used as is, and the moisture content ranged between 10 and 12% on a dry weight basis. The concentrations of starch and polyester were varied to obtain different compositions. At the end of the blending, the total moisture content dropped to 4–5 wt %, on a dry weight basis. For comparison purposes, both blends containing compatibilizers (5 wt % maleated polyester) and physical mixtures (no compatibilizers) were tested.

Sheeting

The sheeting extruder used was a single-screw C. W. Brabender extruder with a length/distance (l/d) ratio of 25:1 and a screw diameter of 1.9 cm. The sheeting extruder was set at 120/130/130/135°C, with the die at the hottest end. The die was a coat hanger die with the following dimensions: entrance diameter, 19.05 mm; die length, 165 mm; and transition zone, 78.87 mm (which abruptly expanded to a width of 152.4 mm). The screw speed was kept constant at 100 rpm. The blend materials were placed in the funnel of the extruder, which was kept almost full at all times. The flow ranged between 80 and 90 g/min. Unless thicker sheets were desired, the die was set to the thinnest gap possible (~ 0.0254 mm). After the sheets exited the die, they passed through chilled rollers. The gap between the rollers (101.6 mm diameter) and the roller speed was adjusted to obtain sheets of various thickness.

Tensile and tear strength

Tensile and tear strength were obtained both in the machine direction (MD) and transverse direction (XD). Tensile strength was obtained by ASTM test method 638 with a SATEC tensile testing machine. Rectangular samples were cut from the sheets and mounted on the grip of a tensile tester. The jaw speed was set at 9 mm/min. Tear strength was determined with a Elmendorf tear tester by test method ASTM 1922-67. The test involved pre-slitting a piece of film sample, followed by measuring the force required for tear propagation. Each composition was replicated, and the results reported are an average of six samples.

Water absorption of blends

The extruded sheet samples were dried in a vacuum oven at 50°C until a constant weight was obtained. These samples were immersed in water at room temperature. The samples were then removed at specific intervals, gently blotted with tissue paper to remove the excess water on the surface, and weighed. This process was repeated at several time intervals. To ensure no leaching had occurred, samples were dried and weighed at the end of the test period, and the end weight was compared with the original sample weight.

Differential scanning calorimetry (DSC)

A Perkin Elmer differential scanning calorimeter (DSC 7) was used to determine the crystallinity of the polymer. Samples of 10 to 15 mg were analyzed in standard aluminum DSC pans under nitrogen atmosphere. Prior to the measurement, the baseline was established using two empty pans. A preliminary scan for the sample was performed before the final measurement. The maximum of the endothermic peak detected on heating scans was taken as the melting temperature, and the peak area was used to calculate the enthalpy of melting with TAS-7 software.

Gel permeation chromatography (GPC)

A Water 150 liquid chromatograph–gel permeation chromatograph (LC–GPC) with a refractive index detector was used to measure the molecular size of starch. A Phenogel (Phenomenex, Torrance, CA) column (300 × 7.8 mm) with 10-mm particle size was used for separation. High-performance liquid chromatography (HPLC) grade dimethyl sulfoxide (DMSO) was used as a mobile phase at flow rate of 1 mL min⁻¹ during analysis. A solution of ~0.2% w/v samples containing a blend of starch was extracted with hot DMSO and filtered through a 0.45- μ m filter to remove insoluble particles. No standard starch samples could be run, so the analysis was based on relative increase or decrease of high/low molecular weight fractions of starch molecules and shift of peak position of the starch component of the blend.

Dynamic mechanical analysis (DMA)

A Rheometrics Mechanical Spectrometer (RMS-800) was used to conduct the DMA to evaluate properties such as loss modulus (G''), storage modulus (G'), and loss tangent ($\tan \delta$). The solid-state rectangular samples were subjected to sinusoidal strain in the torsion mode. The temperature sweep experiments were carried out with 0.04% strain at a frequency of 1.0 rad/s.

The temperature was increased at the rate of 10°C/min.

Wide-angle X-ray scattering (WAXS)

WAXS patterns of the various samples were taken at room temperature with a SIEMENS D5005 X-ray powder diffractometer with nickel-filtered Cu-K α radiation ($\lambda = 0.154$ nm). The rotating anode generator was operated at 45 kV and 40 mA. The scanning regions of the diffraction angle 2θ were 5–35°, with a step size of 0.04 and dwell of 1.0, which covers all the significant diffraction peaks of starch and polyester crystallites. The degree of crystallinity of samples was quantitatively estimated from the relative areas of crystalline and amorphous regions, which were computed by drawing a smooth curve.

Scanning electron microscopy (SEM)

The surface of the sheets were coated with gold/palladium (Au/Pd) alloy by vapor deposition and observed with a JEOL 840II electron microscope.

Surface roughness and waviness

A TENCOR P-10 surface profiler was used to analyze the surface texture (roughness and waviness) of the sheets. A skid-type probe with diamond stylus was used. Roughness average (R_a), the arithmetic average of the absolute values of the profile height deviations, were determined by calculating the area between the trace and the mean height and then dividing this value by the sampling length (5 mm).

RESULTS AND DISCUSSION

Processing

The compositions of the various sheet evaluated are summarized in Table I. The anhydride functional group incorporated onto the polyester backbone by grafting was ~1.0 mol %. Fourier transform infrared (FTIR) studies confirmed the presence of succinic anhydride groups, and nuclear magnetic resonance (NMR) spectra confirmed that succinic anhydride rings are individually attached to the polyester backbone.⁷

The final thickness of the sheets varies with composition. Sheets with higher starch content are thicker than sheets with lower starch content made under similar die and roller conditions. A pure Bionelle sheet is smooth, with a serrated edge. Even a 10% natural sheet has some texture (surface roughness), albeit less than those sheets with a higher natural content. Thicker sheets typically have more texture than thinner sheets of the same composition because the higher

TABLE I
Compositions of Starch/Polyester Sheets^a

Starch	Gluten	Maleated polyester	Bionolle	Tensile strength (MD) ^b	Tensile strength (XD) ^b	Tear strength (MD) ^c	Tear strength (XD) ^c
5	5	0	90	21	21	1716.7	2236.4
5	5	5	85	24	19	1265.6	1134.8
25	5	0	70	18	19	905	1482.6
25	5	5	65	18	23	511.6	870.1
45	5	0	50	11	12	641.9	732.6
45	5	5	45	20	21	460.6	594.8

^a Results are expressed as percentages; each composition has 4 phr of titanium dioxide and 0.01 phr of optical brightener.

^b Tensile strength has units of MPa.

^c Tear strength has units of g/mm.

roller pressure exerted in reducing the thickness of the sheets also tends to smooth the surface. In the absence of rollers, the surface of samples collected directly after they exited the coat hanger die is dependent on the flow rate. At very low or high flow rate, a wavy textured sample with uneven thickness is obtained. There is a narrow range of flow conditions (mass flow rate of 75–85 g/min and torque of 50–75 Nm) that results in unrolled sheet samples of uniform thickness.

Sheets with a natural content of ≥ 30 wt % roll cleaner than sheets of lower natural content because lower natural content sheets tend to stick to the rollers unless the rollers are chilled to temperatures below freezing. At natural contents of 50 wt %, air bubbles are visible due to entrapment of air in the sheet. This entrapment of air occurs because the inherent moisture present in the blends increases as the natural content increases. Depending on the size of the bubbles while passing through the roller, where some stretching occurs, the sheets can become perforated, causing the properties of the sheet to be locally diminished at the location of the perforation.

Tensile and tear strength

The tensile strengths of the sheets are summarized in Table I. At low natural content, the effect of compatibilizer is minimal, as indicated by the similar tensile strengths of the blends with and without compatibilizer. At 50 wt % natural content, the tensile strength of the blends containing compatibilizer is approximately twice that of blends without compatibilizer. Starch is a polymer of anhydroglucose units linked by α -1,4 linkages and is a mixture of two glucan polymers, amylose and amylopectin. Amylose is linear, whereas amylopectin is branched. Starch has a hydroxyl group on the backbone. Proteins, such as gluten, are amino acids linked together by peptide bonds. Irrespective of the protein structure, the end groups of the protein molecules have a carboxyl group at one end and an amine group at the other. The functional groups on the natural polymers are capable of inter-

acting with the anhydride group on the synthetic polymer to form covalent bonds. This capability is true of gluten, which has a primary amino group and is more reactive than the hydroxyl group on the starch backbone.

The tensile strength of sheeted Bionolle ranges between 32 and 35 MPa. The tensile strength of the injection-molded 50 wt % natural blend is 38 MPa,⁸ whereas that of the sheeted blend is 23 MPa. This difference indicates the effect of injection pressure on the tensile properties of blends. The tensile strengths in the machine direction and transverse direction are similar. The effects of amount of compatibilizer on the properties of the sheet are shown in Figure 1. There appears to be minimal effect on the tensile properties at concentrations of ≥ 4 wt %. The properties of samples that went through the roller are no different than those of samples that were collected directly after they exit the coat hanger die.

Tear strengths of the various blends, also summarized in Table I, decrease in both machine and trans-

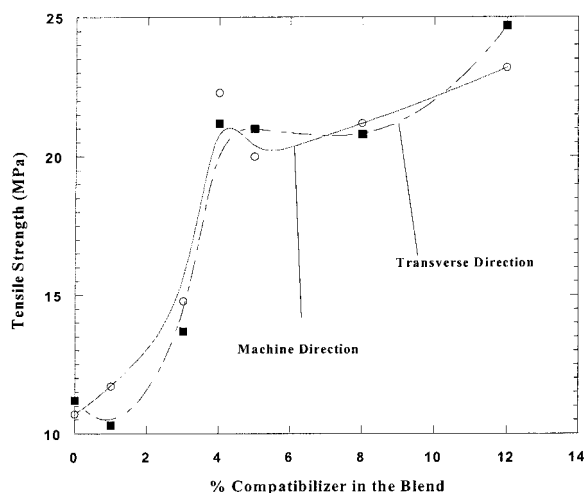


Figure 1 Effect of percent compatibilizer on the tensile properties of the blends. Key: (■) transverse direction; (○) machine direction.

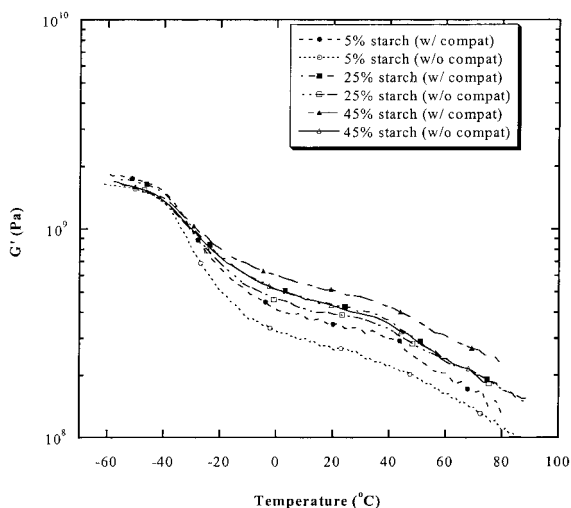


Figure 2 Storage modulus (G') versus temperature for blends at a strain of 0.04% and frequency of 1.0 rad/s.

verse directions as the starch content increases. Another interesting observation is that the tear strengths of anhydride-compatible blends are lower than those of the incompatible blends. This result is in direct contrast to the tensile strength of sheets and tensile and flexural strengths of injection-molded samples.⁸ Elmendorf tear strength is expressed as force per unit thickness of the film, and it is assumed that tear strength has a linear relationship with film thickness. However, in our case, thicker samples have greater tear strength in both machine and transverse directions than thinner samples with the same composition and processing conditions. This result is consistent with observations recorded using polymers.⁹ Also, the samples that went through the roller have higher tear strength than those collected directly after they exited the coat hanger die. This increase in tear strength could be attributed to 'packing effect' encountered during the rolling process, where the sample is compressed due to converging flow. For a given composition and thickness, the tear strength in the transverse direction is greater than that in the machine direction.

Dynamic mechanical analysis

The moisture content in the starch plays an important role in determining the glass transition temperature (T_g) of the starch.¹⁰ The storage modulus (G') values for the various contents of starch in starch/polyester blends with and without compatibilizer are shown in Figure 2. A slightly higher value of G' was observed in blends with high natural content (50 wt %) compared with those for blends with lower natural content (10 wt %). The DMA of different starch content in starch/polyester blends with and without compatibilizer displayed two distinct glass temperature transitions, indicating the phase separation between the blend com-

ponents. The loss modulus (G'') and the loss factor ($\tan \delta$) behavior for the compatibilized and incompatible blends at different natural content are shown in Figure 3. The polyester in the blend showed the first transition between -40 and 10°C , with the peak maximum centered at -26°C . The second transition, corresponding to starch, was observed roughly between 40 and 70°C . The second transition due to starch is not significant because of the low level of starch in the blends. This result is in agreement with earlier studies on other starch/synthetic polymer blend systems.¹¹⁻¹⁴ In these earlier studies, binary blends of starch and polyolefins showed two transitions, whereas a ternary blend of starch/SMA/EPMA showed three transitions, corresponding to each of the three polymers. The appearance of two glass transitions in reactive blends has also been reported by Qin et al.¹⁵ and Chuang and Han.¹⁶

WAXS spectra

The WAXS spectra of various starch content (5, 25, and 45 wt %) in starch/polyester blends with and without compatibilizer show distinct diffraction peaks at 2θ values of 19.6 , 22.7 , and 25.3° and a small peak at 29.1° . The X-ray diffraction peaks of these starch/polyester blends with different starch content appear at the same 2θ values, but an increase in the crystalline phase intensity with decreased starch content in the blend is observed. The degree of crystallinity of these starch/polyester blends was measured from the relative areas of crystalline and amorphous regions, which were computed by drawing a smooth curve.¹⁷ The calculated degrees of crystallinity of different starch content with and without compatibilizer in the blend are shown in Table II. The degree of crystallinity of the blends with different starch contents decreases from

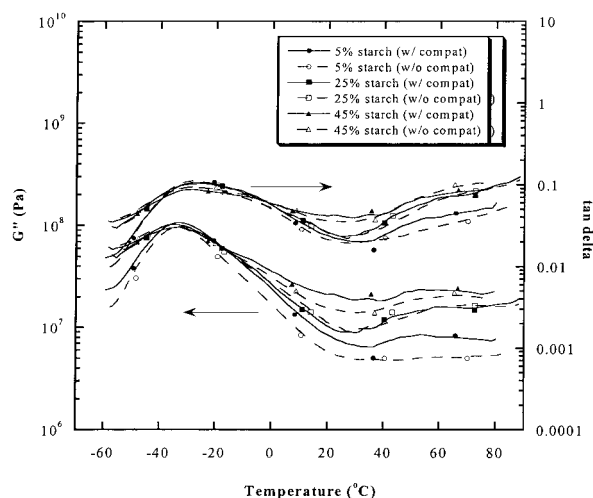


Figure 3 Loss modulus (G'') and $\tan \delta$ versus temperature for blends at a strain of 0.04% and frequency of 1.0 rad/s.

TABLE II
Degree of Crystallinity of Starch/Polyester Sheets

Starch content in the blend (wt %)	Degree of crystallinity (%)	
	With compatibilizer	Without compatibilizer
5	49.2	50.7
25	39.6	42.2
45	35.9	36.1

49.2 to 35.9% as the starch content increases in the blend from 5 to 45 wt %. Also, the degree of crystallinity is not affected by the presence of the compatibilizer. The degree of crystallinity of the pure polyester is 41.5%. High natural content in the blend leads to higher torque and stresses and, hence, more destruction of starch crystallites. In the case of low natural content in the blend (5 wt %), the torque and stresses are low and, therefore, the destruction of starch crystallite structure is minimal.

Scanning electron microscopy

SEM was used to analyze the blend morphology of the starch/polyester blends with various starch content (10, 30, and 50 wt %). The SEM photographs of various starch content in the starch/polyester blends with and without compatibilizer are shown in Figures 4–6. A granular arrangement of the starch within the polymer matrix is evident in these photographs. In the natural state, starch exists in a granular form, and its size and shape depend on the origin. Generally, native corn starch consists of spherical or ellipsoidal granules that vary in size from 5 to 25 μm .¹⁸ Starch behaves like thermoplastic material at high shear and high moisture (>10%), whereas at low moisture content of <10%, starch granules may melt, leading to some degradation and/or debranching when subjected to high shear. Also, the starch/synthetic polymer blends contain a mixture of molten starch and polymer and unmelted or partially melted starch granules. The properties of these blends depend on their phase morphology and the interfacial adhesion between the starch and synthetic polymer phases. The extent of starch melting and degradation/debranching during thermomechanical processing depends on the moisture content, melt temperature, extruder screw speed, and screw configuration and affects the final properties of the blends.^{19, 20} The starch granules do not undergo complete melting under the conditions employed in this study. Thus, we have both a molten phase of starch and a synthetic polymer in which unmelted or partially melted starch granules are imbedded. The SEM photographs of a blend containing 5 wt % starch with compatibilizer (Fig. 4a) and without compatibilizer (Fig. 4b), reveal a granular arrange-

ment of starch within the polyester matrix. The presence of discrete particles indicates unmelted and homogeneously dispersed starch granules throughout the synthetic polymer matrix. The size of the starch granules in the blends is $\sim 10\text{--}25\ \mu\text{m}$. It is also evident that the melted starch granules (dark phase) are formed in a co-continuous phase with the synthetic polyester matrix. Similar morphology (phase structure) is observed in the blends containing 25 and 45 wt % starch with compatibilizer (Figs. 5a and 6a) and without compatibilizer (Figs. 5b and 6b). The effect of

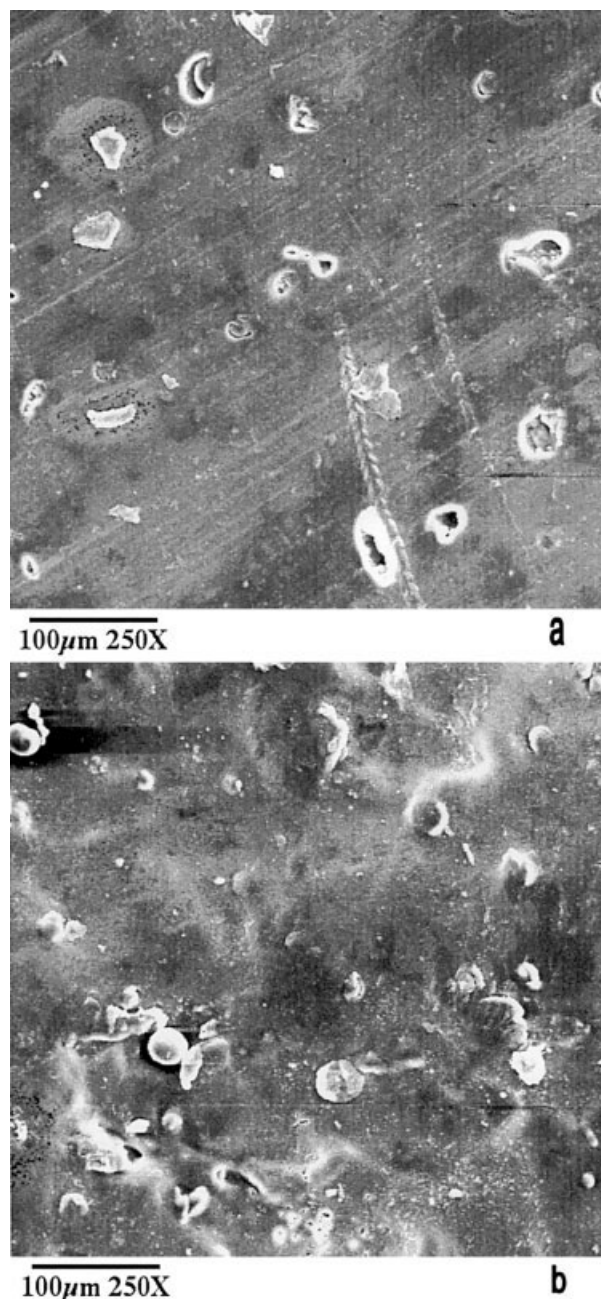


Figure 4 Scanning electron micrographs of starch/polyester blend containing 5 wt % starch (a) with compatibilizer and (b) without compatibilizer.

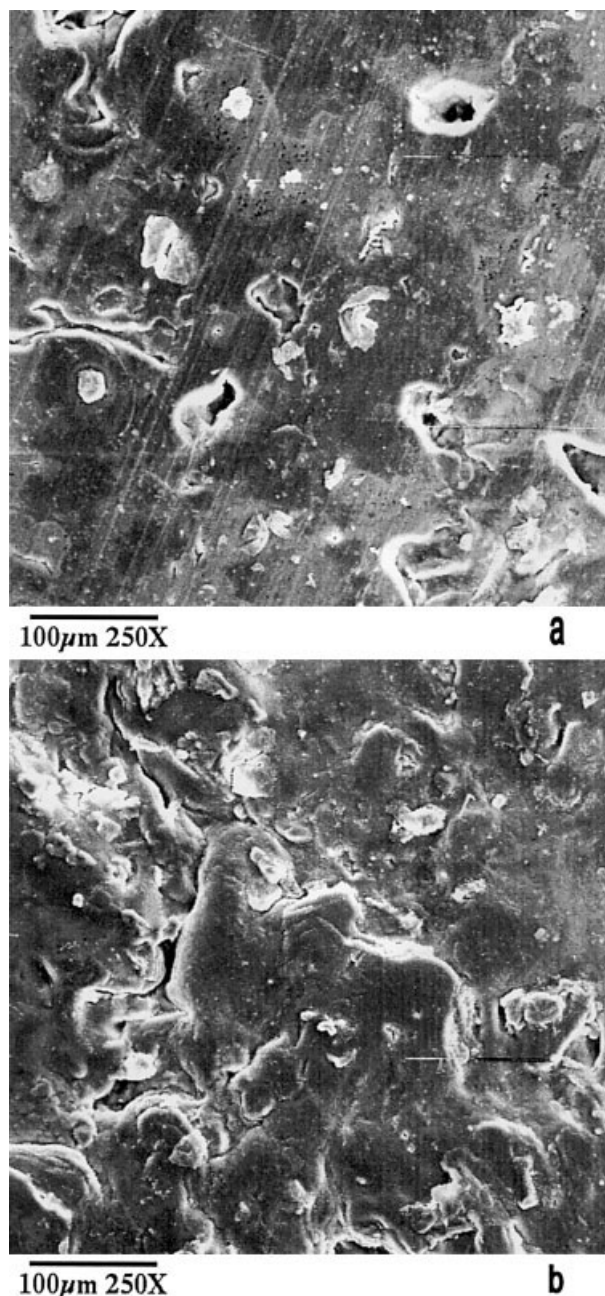


Figure 5 Scanning electron micrographs of starch/polyester blend containing 25 wt % starch (a) with compatibilizer and (b) without compatibilizer.

compatibilizer for 10 wt % natural content blend is indistinguishable (Figs. 4a and 4b). However, at 30 and 50 wt % natural content, the compatibilized blend shows a well dispersed starch in a continuous polyester phase. This result is in agreement with other studies on blends of starch and synthetic polymers, indicating that some of the starch blended with the thermoplastics maintains its granular shape despite the action of the shear forces during processing^{19,20}. This result indicates that the dispersion of starch in blends with other thermoplastics plays a crucial role in the eventual properties attainable by the blend.

Water absorption

Water absorption data for the sheets are shown in Figure 7. Water absorption depends on the polymer-solvent miscibility and on the existence of interactions between water molecules and polar groups present in the polymer. Because both starch and proteins are hydrophilic, as the natural content increases, the percent water absorption increases. There is a sharp initial burst of water uptake, which is accomplished in the first day of the experiment. It ranges from 43% of the initial weight for 10 wt % natural content to 77% of the

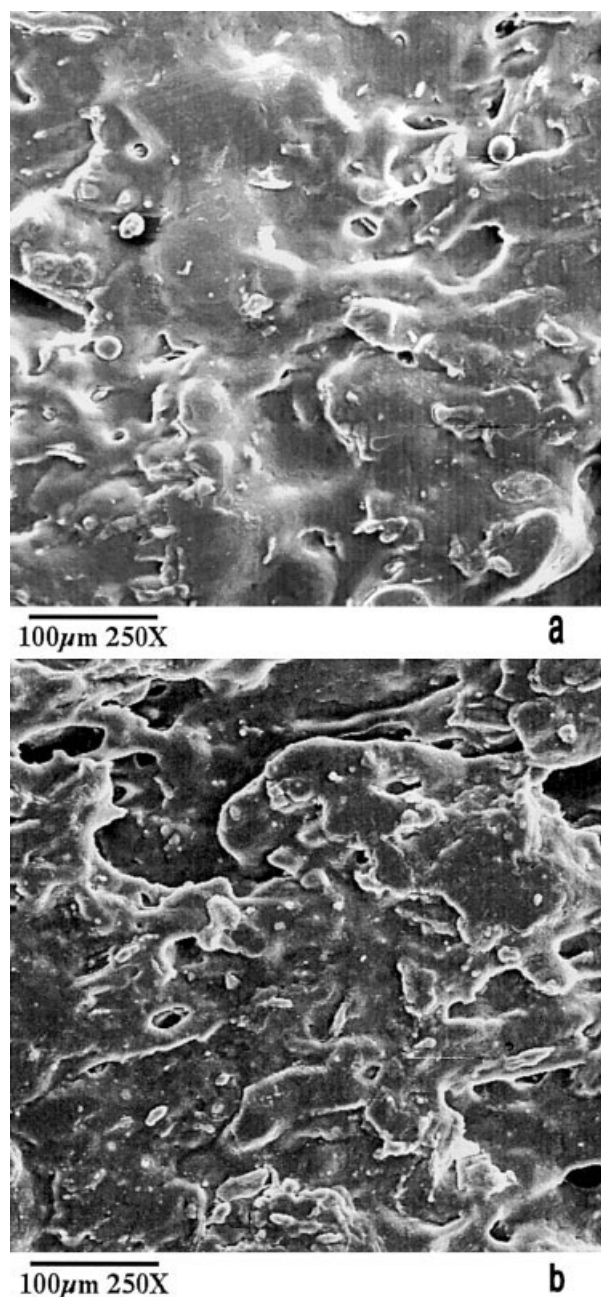


Figure 6 Scanning electron micrographs of starch/polyester blend containing 45 wt % starch (a) with compatibilizer and (b) without compatibilizer.

initial weight for the 50 wt % natural content. The initial burst of water uptake $[M(t)/M_\infty]$, where M_∞ is the equilibrium moisture content] for all the blends were found proportional to $t^{0.5}$, followed by a leveling off and approaching an apparent equilibrium value. The water uptake is proportional to $t^{0.5}$ for blends containing 10 and 30 wt % of natural content for $t < 10$ days. Hence, the initial water uptake mechanism can be considered to be diffusion controlled.²² This assumption is consistent with the observation of Alfrey²³ that when the material is below the T_g , the exponent n has a value close to 0.5.

The initial water uptake is the water diffusing into the amorphous regions of the material. Water absorption is due to interactions with functional groups on the polymer chains as well as capillary effects. However, in the case of sheeted blends, capillary effects are expected to be minimal because of the pressure involved during the processing. The water molecule interacts with the hydroxyl group in starch or the amino and carboxyl groups in proteins. As the starch content increases (protein content is kept constant at 5 wt %), the starch undergoes increased melting, making an increased number of hydroxyl groups available for interaction with the water molecules.

Differential scanning calorimetry

The thermal properties (e.g., melting, enthalpy) of these starch/polyester sheets were evaluated by DSC. The pure polyester has a melting endotherm at 117°C, with an enthalpy of 60.0 J/g. The starch used in this study has a melting endotherm at 116°C, with an enthalpy of 143.5 J/g. The starch/polyester sheets show endothermic peaked at ~110–114°C. These melting endotherms are observed in approximately the same temperature ranges, irrespective of the sheet

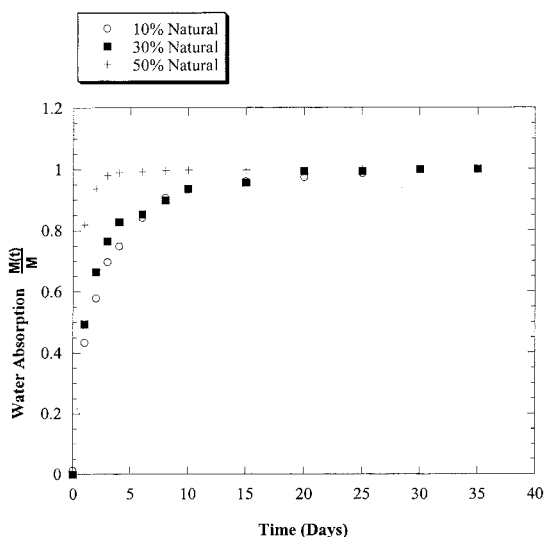


Figure 7 Water absorption of blends as a function of time.

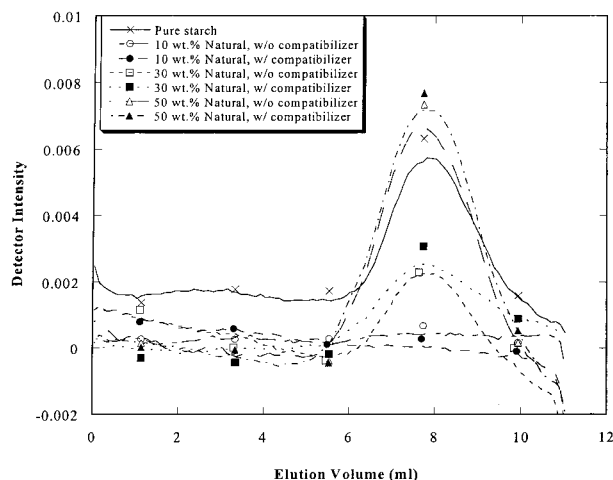


Figure 8 Gel permeation chromatographs of starch moieties in the blends.

composition (natural content of 10, 30, and 50 wt %) and the sheeting conditions. However, the melting enthalpy decreases with increases in natural content from 10 to 50 wt % in the sheets. The melting enthalpies of 10, 30, and 50 wt % natural content in the sheets are 65.8, 49.2, and 27.7 J/g, respectively. The decrease in enthalpy for blends containing higher natural content is primarily due to the increased melting of starch granules caused by the higher stresses generated as a result of increased viscosity. This decrease in enthalpy leads to increased destruction of starch crystallites compared with pure starch. These results are in agreement with the WAXS results.

Gel permeation chromatography

The gel permeation chromatographs of pure starch and compatibilized and uncompatibilized polyester sheets containing natural contents of 10, 30, and 50 wt % are shown in Figure 8. The chromatograms of polyester sheets with 50 wt % natural content processed at different conditions are shown in Figure 9. All these chromatograms have a peak position at approximately the same position, irrespective of the sheet composition and the sheeting conditions, indicating that the fragmentation/degradation of starch during the process is minimum or negligible. This result is in contrast to our earlier presented results, where starch moieties underwent significant degradation during processing. The apparent shear rate experienced in the coat hanger die, estimated to be $<1 \text{ s}^{-1}$ (calculated using equations for flow through slits), is several orders of magnitude lower than that experienced during injection molding. It is well known²⁴ that under high shear conditions, starch moieties experience degradation because of the high stress experienced during processing. Thus, sheeted products are likely to be less sensitive to moisture pick-up than injection-molded products.

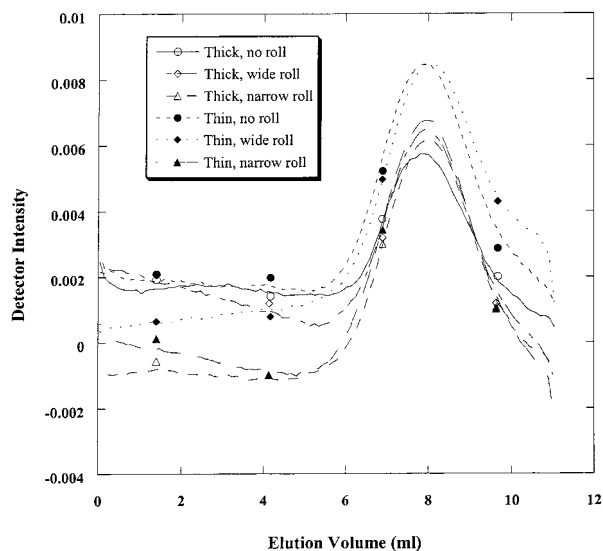


Figure 9 Gel permeation chromatographs of samples with 50 wt % natural content processed under different sheeting conditions.

Surface roughness and waviness

The surface roughness and waviness of the various samples are summarized in Table III. The texture of the surface (i.e., deviation from nominal surface) is affected by a combination of longer wavelength waviness and shorter wavelength waviness. Roughness is affected by the process conditions as well as the nature of the processed materials. In printing applications, surface properties such as roughness affect friction and adhesion.

As the natural content increases, the roughness and waviness increase. Also, the more narrow the roller gap and die height, the smoother the surface (Table IV). A higher natural content blend also contains higher moisture, which leads to surface irregularities because the material is processed at temperatures $>100^{\circ}\text{C}$. Furthermore, materials with higher natural content tend to have higher viscosities²⁵ and higher residual stresses²⁶ and tend to relax less.²⁷ The instabilities are thought to occur when the shear stress exceeds a critical level, similar to the sharkskin effect observed during the extrusion of polymer melts.²⁸ Another problem is the potential presence of extrudate swell due to the first normal stress difference.

TABLE III
Roughness and Waviness of Polyester Sheets with Various Natural Content

Natural polymer content (wt %)	Roughness, Ra (μm)	Waviness, Wa (μm)
0	0.049	0.246
10	0.31	0.769
30	0.642	1.512
50	1.42	9.243

TABLE IV
Roughness and Waviness of Polyester Sheets with Different Processing Conditions

Die gap and roller gap	Roughness, Ra (μm)	Waviness, Wa (μm)
Thin and no roll	1.441	9.008
Thin and wide roll	1.253	5.114
Thin and narrow roll	1.076	4.692
Thick and no roll	1.874	33.521
Thick and narrow roll	1.501	12.621

Extrudate swell can also cause the appearance of edge bead, a thickening of the web at its outer edges that is several times thicker than the center of the web. Application of roller pressure reduces the surface irregularities. By carefully controlling the die and roller thickness, the roughness and waviness are reduced. Another avenue of reducing both the roughness and waviness is passage through multiple sets of rollers. The 50 wt % natural content blend produced in a commercial calendaring produced waviness and roughness of 0.249 and 0.067 μm , respectively.

CONCLUSIONS

Blends of natural and synthetic polyesters can be processed into sheets. However, the flow rate needs to be controlled because it leads to process instability. At low natural content (<30 wt %), the effect of compatibilizer is minimal. There is a decrease in tensile strength between the blends containing natural polymer and those of the pure synthetic polymer. This result is in contrast to injection-molded samples for which the tensile strengths of the compatibilized blends are similar to those of the synthetic polymer.²⁸ The difference is primarily due to the packing process experienced during injection molding. The tear strength decreases as the starch content increases, and this decrease is higher for compatibilized blends. The blends form a two-phase system as evidenced by SEM and DMA results.

Blends containing compatibilizers are more homogeneous than those without compatibilizers. Water absorption displays Fickian diffusion and increases with increases in natural content. As the natural content increases, the degree of crystallinity and the melting endotherm decrease due to the increased melting of starch granules. GPC results indicate minimal degradation of starch molecules compared with injection-molded samples because of the lower stresses generated during the sheeting process. As the natural content increases, the surface roughness and waviness of the sheets increase.

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