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Processing and characterization of thermoplastic starch/polyethylene blends

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The behaviour of gelatinized starch plasticized with glycerol (also known as thermoplastic starch (TS)) is studied as the dispersed component in a polyethylene (LDPE or LLDPE) matrix. A processing technique was developed to compound the blends in one continuous process in a co-rotating twin-screw extruder fed by a single-screw extruder. The use of the single-screw as a side feeder allowed for gelatinization of the starch before feeding it into the twin-screw at controlled temperature and pressure. The screw configuration of the twin-screw extruder maintained high pressure ($\geqslant 0.9$ MPa) during blending to prevent early evaporation of water. These materials displayed morphological characteristics typical of immiscible polymer–polymer blends. The number-average diameter of the dispersed phase increased from 4 μm with 8 wt% TS to 18 μm with 36 wt% TS in LDPE blends. It ranged from 3 to 8 μm in LLDPE blends containing 7 to 39 wt% TS. These results therefore indicate the possibility of achieving a level of morphological control with respect to the size and shape of the dispersed phase in these systems. Dry granular starch, on the other hand, typically is dispersed as a spherical like particle with a fixed morphology of approximately 10 μm. The blends in this study, at high TS loadings, demonstrate high elongational properties at break even without addition of an interfacial modifier. The LDPE blend containing 22% TS had 240% elongation at break and its modulus was 109 MPa. The LLDPE blend containing 39% TS had more than 540% elongation at break, while the modulus was 136 MPa. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: blend; thermoplastic starch; gelatinization polyethylene; morphology; tensile properties)

INTRODUCTION

Starch is a blend of amylose and amylopectin, both of which are polysaccharides composed of α-D-glucopyranosyl units, $(C_6H_{10}O_5)_x$[1]. Native starch granules swell when they absorb water through hydrogen bonding with their free hydroxyl groups, but they still retain their order and crystallinity. However, when these swollen starch granules are heated, hydrogen bonding between adjacent glucose units is disrupted. The crystallinity is progressively destroyed. This process is called gelatinization[1,2]. The processing of starch and water in a heated extruder is an efficient way to obtain gelatinized starch[2]. High shear can be generated in the extruder to disrupt the starch granules. The pressure generated raises the boiling point of water so that higher temperatures are attainable for rapid and complete disruption of the granular structure.

Starch is an inexpensive, renewable, and natural polymer. It can be blended with synthetic polymers to lower the cost and to confer partial environmental degradability to the blends. Addition of dry starch granules to low density polyethylene (LDPE) follows the general trend of filler effects on polymer properties[3–8]. The modulus increases due to the stiffening effect of the granules and the elongation decreases as the starch content is increased. There have been few reports on gelatinized starch/synthetic polymer blends. Such materials should have different properties from composites incorporating native starch granules. Otey and co-workers[9,10] developed gelatinized starch–plastic material films containing gelatinized starch with 6–10% moisture. These were complex systems containing gelatinized starch, poly(ethylene-*co*-acrylic acid) (EAA), LDPE, urea and ammonium hydroxide. The urea promoted gelatinization of starch at low water levels[11]. Ammonium hydroxide acted as a linkage agent between the hydrophilic starch and the hydrophobic LDPE[11]. The optimum composite was made of (wt%) 40% starch, 25% EAA (80 wt% ethylene), 25% LDPE and 10% urea[12]. The ultimate tensile strength of the optimum composite was 9 MPa and its elongation at break 42%. The ultimate strength was similar to that of EAA itself. Elimination of the polyethylene improved the properties of the composite[12,13]. It was concluded that gelatinized starch acted as a rigid filler in the films thus reducing the elongation[13].

In other studies it was found that the ductility of gelatinized starch plasticized with approximately 15 wt% glycerol and 10 wt% water (called thermoplastic starch) was improved by the addition of poly(ethylene-*co*-vinyl alcohol) (44 mol% ethylene) (EVOH)[14]. The addition of glycerol lowers the modulus of thermoplastic starch[15]. The blends exhibited lower modulus, lower tensile strength at break, and higher elongation at break than

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the pure, plasticized, thermoplastic starch (TS). TS/EVOH blends containing ≥50 wt% EVOH showed almost as high an elongation at break as neat EVOH.

Multiphase systems using dispersed gelatinized starch plasticized with glycerol should have better elongational properties at break than those with dispersed dry starch granules. Furthermore, a mixture of such thermoplastic starch and polyethylene could potentially behave in a manner similar to more conventional polymer–polymer blends. This would allow greater control of the dispersed phase morphology since the thermoplastic starch should undergo deformation, disintegration, and coalescence. In this study the processing, morphology, and tensile properties of thermoplastic starch/polyethylene blends have been investigated.

EXPERIMENTAL

Materials

Two commercial grades of polyethylene (PE) pellets were used: (1) LDPE PE 2040 (Rexene Chemical Co.) with an ASTM melt index of 12 g (10 min)$^{-1}$ and a density of 0.92 g cm^{-3}; (2) linear low density polyethylene Dowlex 2535 (LLDPE, Dow Chemical Co.) with an ASTM melt index of 6 g (10 min)$^{-1}$ and a density of 0.92 g cm^{-3}.

Supergell 1203-C wheat starch powder from ADM/Ogilvie was composed of 25 wt% amylose and 75 wt% amylopectin. The moisture level was 10%. Glycerol (99.5 vol%), which was obtained from Biopharm Corporation, was used as a plasticizer. Distilled water was used for gelatinization.

Processing

Prior to processing, 48% starch, 33% glycerol, and 19% water were mixed for 15 min in a Hobart type mixer. The mixture was then left to stand for 1 h to allow the starch granules to swell. The starch/water/glycerol suspension was converted into TS by processing in a single-screw extruder.

A combination single-screw and twin-screw extruder (*Figure 1*) was used to blend the PE and TS. The single-screw extruder had a screw length to screw diameter ratio, *L*/*D*, of 26, a length of 495 mm, and a compression rate of 2. The co-rotating twin-screw extruder LSM 30.34 (Leistritz AG) had a *L*/*D* of 28 and a screw length of 960 mm. The twin-screw extruder was sectioned into eight zones. An adapter connected the exit of the single-screw extruder to the twin-screw extruder at the fourth zone. The PE was fed into the hopper at the first zone, and the TS was fed in via the single-screw extruder. The screw configuration in the twin-screw extruder allowed melt blending under pressure in zone four, while preventing evaporation of water at that point (*Figure 2*). Blending continued in zones five and six. The volatilized water escaped the twin-screw extruder in the seventh zone which was equipped with an open window (40 x 62 mm). The vapour of an aqueous solution of glycerol contains significantly more water than glycerol at 150°C[16]. Glycerol would therefore remain in the starch to a larger degree. The blend was extruded through a rectangular die of dimensions 3.5 x 32 mm. The extrudates were cooled between two water-cooled, steel rolls with a gap of 2 mm to freeze-in the morphology. Take-up speed was set as low as possible to minimize further modification of morphology due to axial tension.

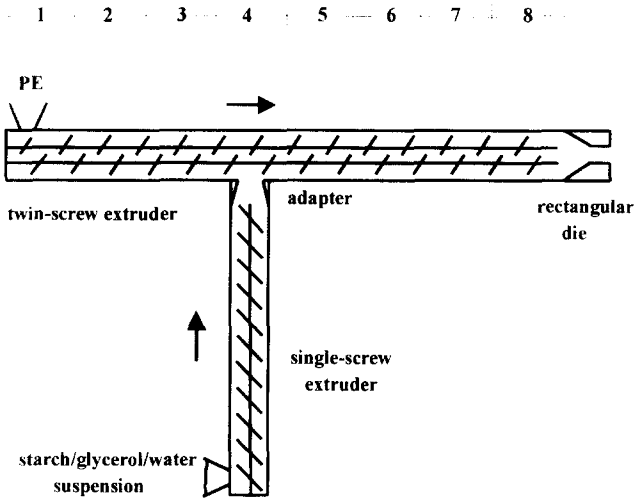


Figure 1 Diagram of the combined co-rotating twin-screw extruder and single-screw extruder

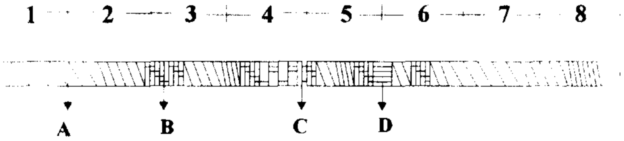


Figure 2 Screw configuration used for the twin-screw extruder, extrudate entered in zone 4. A, transport element; B, right-handed kneading block; C, shearing disk; D, restrictor

During blending, the temperature of the barrel of the twin-screw extruder was maintained at 150°C. The temperature profile of the barrel of the single-screw extruder was set at 70°C at the feeder and 90°C at the adapter. The screw speed of the single-screw extruder was varied to modify the content of TS in the blends. The blends containing LDPE were processed at 150 rpm and at a flow rate of 128 g of LDPE min^{-1} in the twin-screw extruder. The blends containing LLDPE were processed at 125 rpm and 110 g of LLDPE min^{-1}. The temperature and the pressure of the melt in the adapter were measured with a type J thermocouple and a pressure gauge. Both were recorded with a computer data acquisition system. The temperature measured was 95°C, and the pressure varied between 0.9 and 2.3 MPa with the screw speed of the single-screw extruder. Unblended TS plasticized with glycerol was processed in the combined single-screw, twin-screw extruders under the same conditions as above except that the temperature of the barrel of the twin-screw extruder was set at 90°C. After processing, the blends and the TS were stored in sealed PE bags at 4°C until further analysis.

Analysis

Electron microscopy. A JSM-820 scanning electron microscope (SEM, JEOL) was used to observe the size and shape of the dispersed phase in the TS/PE blends. The TS/PE blends were microtomed under liquid nitrogen to create a plane face using a Leica model Jung RM 2065 microtome equipped with a glass knife. Samples with surfaces longitudinal and transverse to the machine direction were prepared. During and prior to microtoming, samples were frozen in a flow of liquid nitrogen to reduce the degree of surface deformation. Prior to microscopy, samples were coated with a gold/palladium alloy.

Image analysis. A Jandel digitizing tablet controlled by the Jandel Sigma-Scan system was used to measure the area (A) and the perimeter (P) of the dispersed phase. In this study 200 droplets were measured for each sample. In the case of elliptical particles the diameter reported is for the equivalent sphere. A correction was applied to the distribution of diameters for each sample according to the Saltikov method[17,18], and the volume-average (d_v) and number-average (d_n) diameters were calculated. A form factor, $F = 4\pi A/P^2$, was calculated to quantify the deformation of the dispersed phase and was the average of 180–200 droplets. For a spherical particle, $F = 1$; for maximum deformation, $F = 0$ (ultrathin fibre of vanishing diameter).

Thermogravimetry. A TGA 2950 (TA Instruments) equipped with a Thermal Analysis 2000 computer control/data acquisition system was used. The samples were heated at 10°C min^{-1} from 25 to 200°C.

Differential scanning calorimetry. Differential scanning calorimetry (d.s.c.) was performed on a 910 DSC (Dupont Instruments) equipped with a Thermal Analysis 2000 computer control/data acquisition system (TA Instruments). The samples (10–20 mg), encapsulated in d.s.c. aluminium pans, were heated at a rate of 10°C min^{-1} from 25 to 200°C.

Capillary rheometer. A capillary rheometer was used to measure the viscosity of the PE at high shear rates similar to that experienced on the twin-screw extruder at 150°C (*Figure 3*). Capillaries with $L/D = 5$, 10, and 20 were used. The Bagley correction and the Rabinowitsch analysis were applied to calculate the viscosity *versus* shear rate from the experimental data.

Plate–plate rheometer. A Bohlin model VOR rheometer having a Couette geometry was used to measure the viscosity of the suspension of starch, glycerol, and water. The viscosity was measured as a function of the shear rate for a complete cycle at 25°C (*Figure 4*).

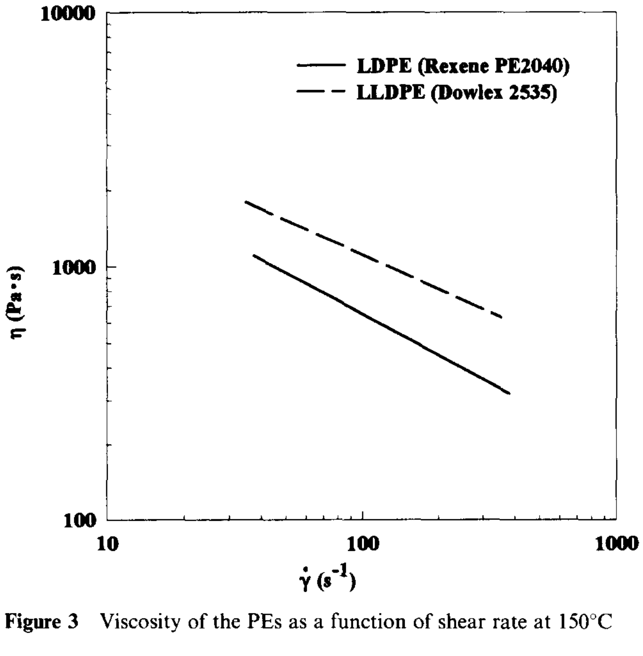


Figure 3 Viscosity of the PEs as a function of shear rate at 150°C

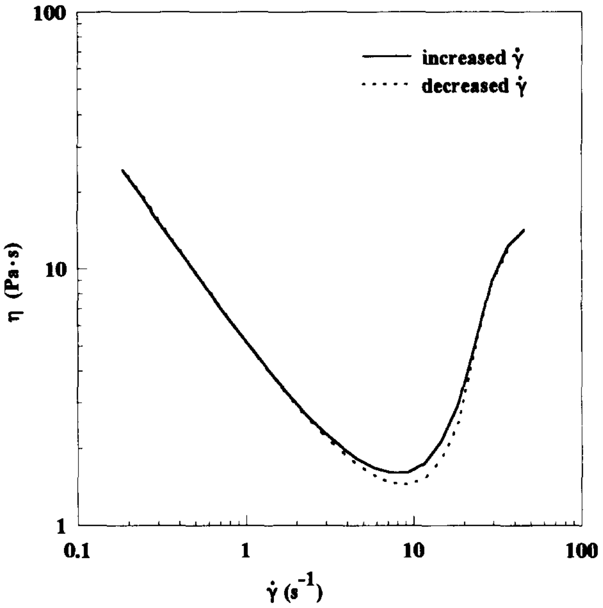


Figure 4 Viscosity of the starch/glycerol/water suspension as a function of shear rate at 25°C

Tensile testing. Tensile testing followed the ASTM D-638 method. Tests were performed on a M30K machine (JJ Instruments) equipped with a cell of 100 Newtons and a data acquisition system. Samples were strained at a rate of 10 mm min^{-1} with an initial grip distance of 25 mm. Data were recorded at a frequency of 5 Hz. Between 5 and 10 samples were tested for each blend. The average values of the Young's modulus (tangent modulus) (E), ultimate tensile stress at yield (σ_y), elongation at yield (ϵ_y), and elongation at break (ϵ_b) were calculated. The variations were reported as the standard deviation of the samples.

Tensile specimens of type III were cut longitudinally from extruded sheets. Sheets having a thickness of 2 mm were compression moulded to 1.7 mm in a Carver press. Prior to moulding, the sheets were heated at 150°C between the platens for 1 min. 20 kN was applied for 30 s followed by 40 kN for 30 s.

RESULTS AND DISCUSSION

Previous work[19,20] had shown that, in an internal mixer, rapid water loss resulted in great variation in the physical properties of the gelatinized starch produced. To minimize this problem, a processing technique was developed that incorporated a single-screw extruder brought in midway to a twin-screw extruder. In the following sections the processing, morphology, thermal analysis, and tensile properties will be considered.

Processing

PE was processed at a constant flow rate in the twin-screw extruder. Both the composition of thermoplastic starch (C_{TS}) and the pressure in the adapter increased as the screw speed of the single-screw extruder was increased (*Figures 5* and *6*). C_{TS} was calculated from

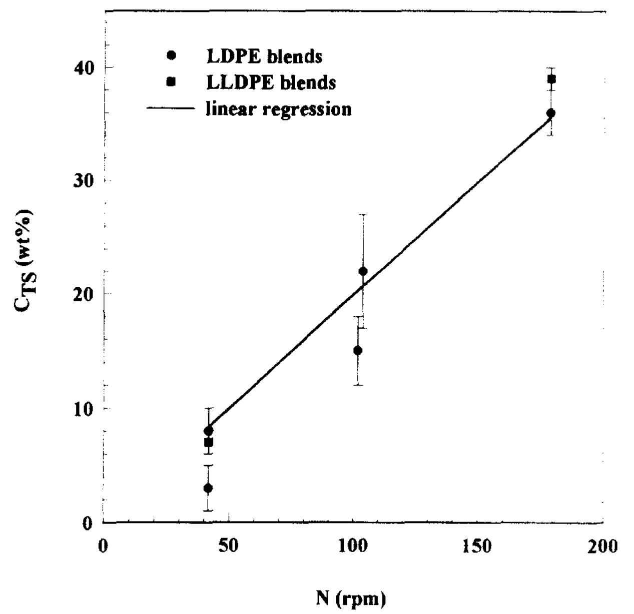


Figure 5 Composition of TS as a function of single-screw extruder screw speed

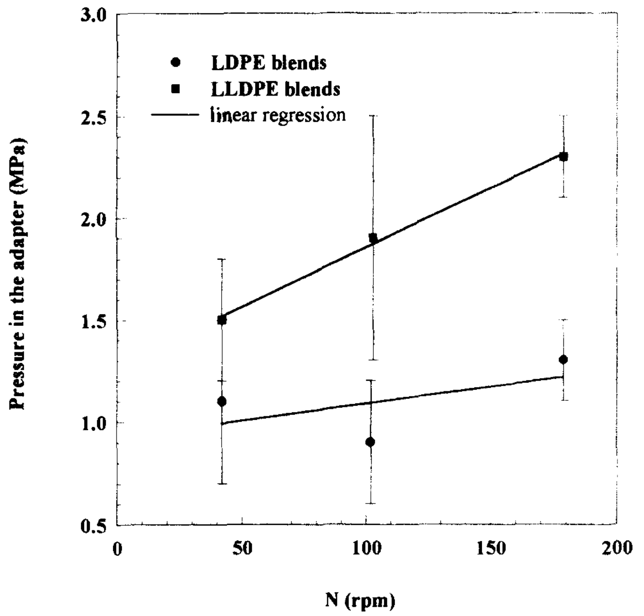


Figure 6 Pressure in the adapter as a function of single-screw extruder screw speed

the extrudate flow rate minus the polyethylene flow rate and hence included everything but PE (i.e. starch, glycerol, and remaining water). Its accuracy was confirmed by thermogravimetric analysis (t.g.a.) for the LDPE blends (*Figure 7*). The t.g.a. weight loss values shown were calculated by estimating the difference in weight loss between 350 and 600°C. The relationship between the composition of TS and the screw speed appeared to be linear (*Figure 5*). The pressure was always maintained at greater than 0.9 MPa during the processing of all the blends to prevent boiling of the water and glycerol mixture.

The starch/glycerol/water suspension is a shear-thickening fluid at a shear rate higher than $10\,s^{-1}$ at 25°C (*Figure 4*). The flow of a shear-thickening fluid of this type is not well understood and may be the cause of variations of the flow rate of the suspension, TS composition/screw speed and pressure/screw speed.

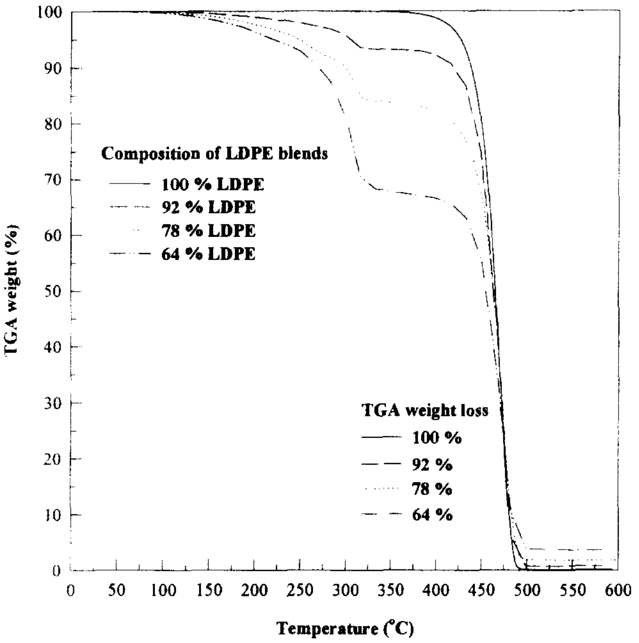


Figure 7 T.g.a. of blends containing TS and LDPE: composition values shown on the left are calculated from flow rate data; values on the right are calculated from t.g.a. weight loss

Morphology/thermal analysis

TS/LDPE and TS/LLDPE blends were immiscible but behaved as polymer blends composed of two deformable phases as seen by the size and the shape of the thermoplastic starch domains in the LLDPE (*Figures 8a, 8b, 8c* and *8d*). The size of the dispersed phase varied with the composition of TS in the blends but were similar in the longitudinal and transverse directions. Native wheat starch granules are typically spherical in shape with a diameter of approximately 10 μm. Thus the starch was effectively gelatinized (*Figure 8e*). The TS was a continuous material that was deformed and dispersed in the polyethylene during processing.

Additional confirmation of starch gelatinization is shown by d.s.c. analysis of TS recovered after processing only in the single-screw extruder (*Figure 9a*). The TS, unblended with PE, showed an endothermic heat flow at the same temperature as a weight loss measured by t.g.a. between 122 and 180°C (*Figure 9b*). The large peak in the d.s.c. analysis was therefore due to the evaporation of volatiles such as glycerol and water still in the TS at that time during processing. Gelatinization of wheat starch with water occurs within the range 65–125°C[2,21]. Any ungelatinized starch would have produced an endothermic peak in that range, but there was none (*Figure 9a*), indicating that complete gelatinization had already been achieved.

The system displays several of the basic characteristics of a polymer blend. For example the number- and volume-average diameter of the dispersed phase (d_n and d_v) increased with the quantity of TS (*Table 1*). The distribution of the size (d_v/d_n) also broadened with composition. The sizes in the longitudinal and transverse direction were not very different at the same compositions. Previous work on the influence of the

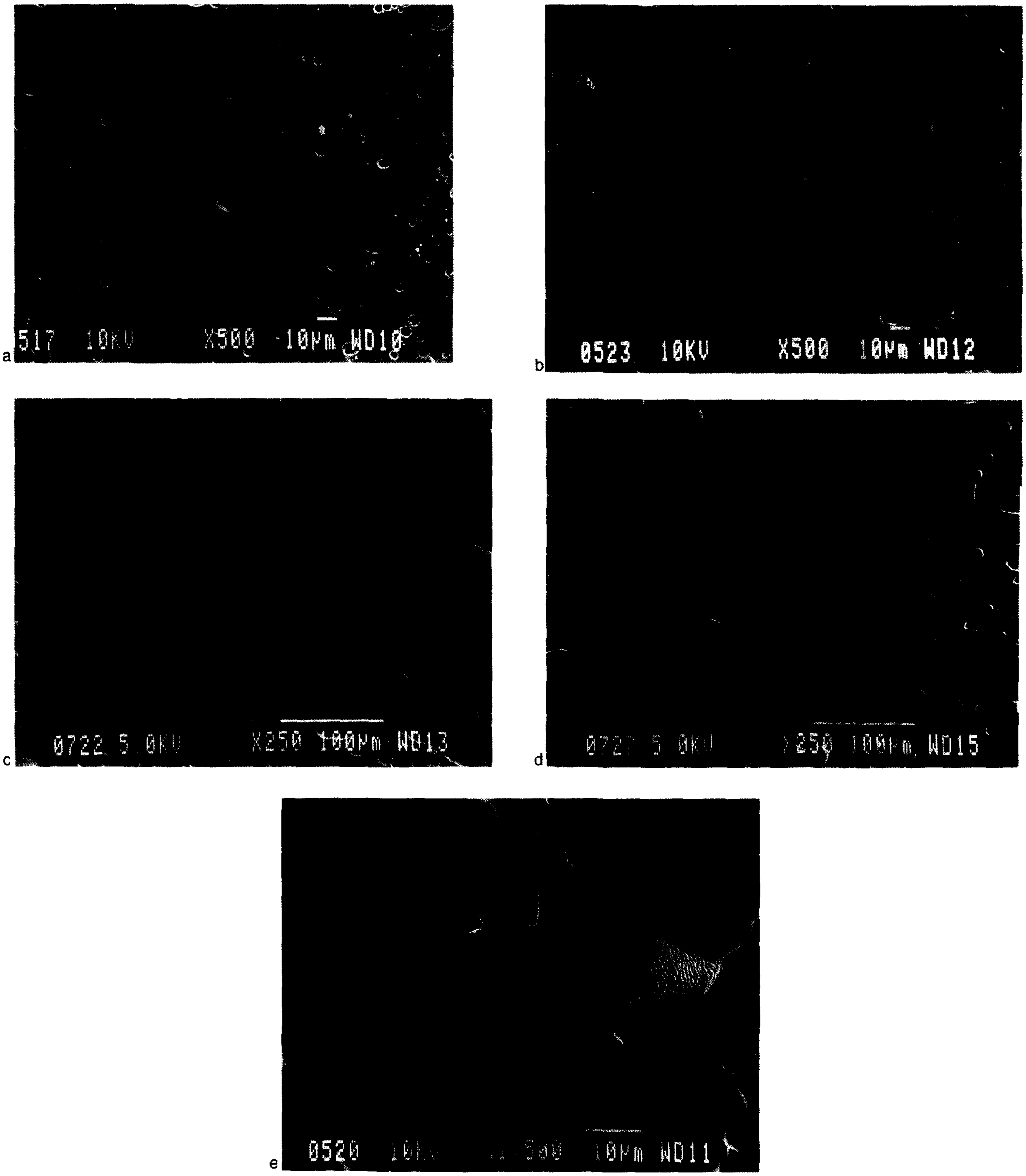
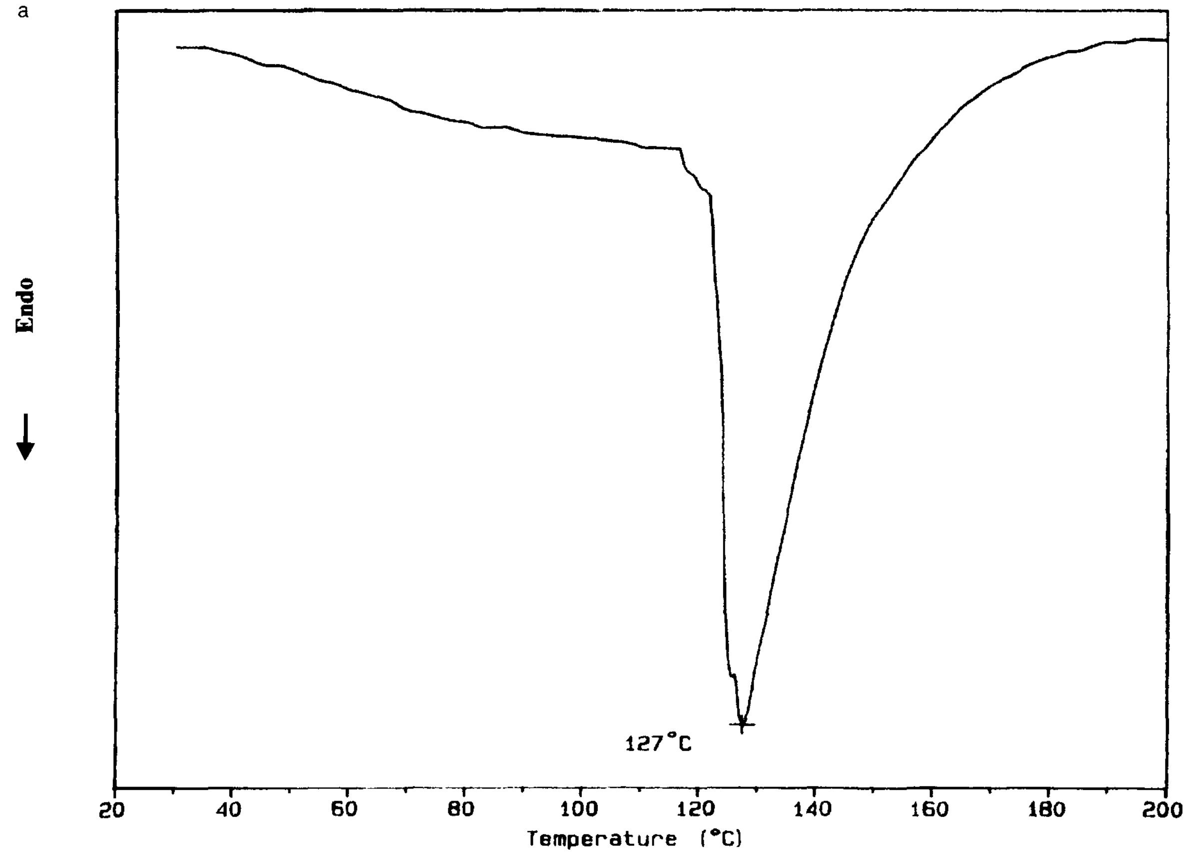


Figure 8 SEMs of TS/LLDPE blends: (a) 7% TS in the transverse direction; (b) 7% TS in the longitudinal direction; (c) 39% TS in the transverse direction; (d) 39% TS in the longitudinal direction; (e) continuous and deformable TS dispersed phase from a cryogenic freeze fracture

composition on the size of dispersed phase in blends processed in a twin-screw extruder showed the same tendencies[22]. In the present work blends containing LLDPE displayed smaller particle sizes than the blends containing LDPE probably because the viscosity of LLDPE is higher than the viscosity of LDPE (*Figure 3*). In previous studies a high viscosity ratio of the blend has been shown to increase the size of the dispersed phase[22,23].

The dispersed phase showed some biaxial deformation as evidenced by SEM photos taken in the transverse direction (*Figures 8a* and *8c*) and was elongated in the longitudinal direction (*Figures 8b* and *8d*). A degree of biaxial deformation was applied to the melt as it went through the die and as it was drawn through the calendar rolls. The dispersed phase was spherical in the transverse direction at low composition of TS. The form factor (F) was 1 at low TS composition and



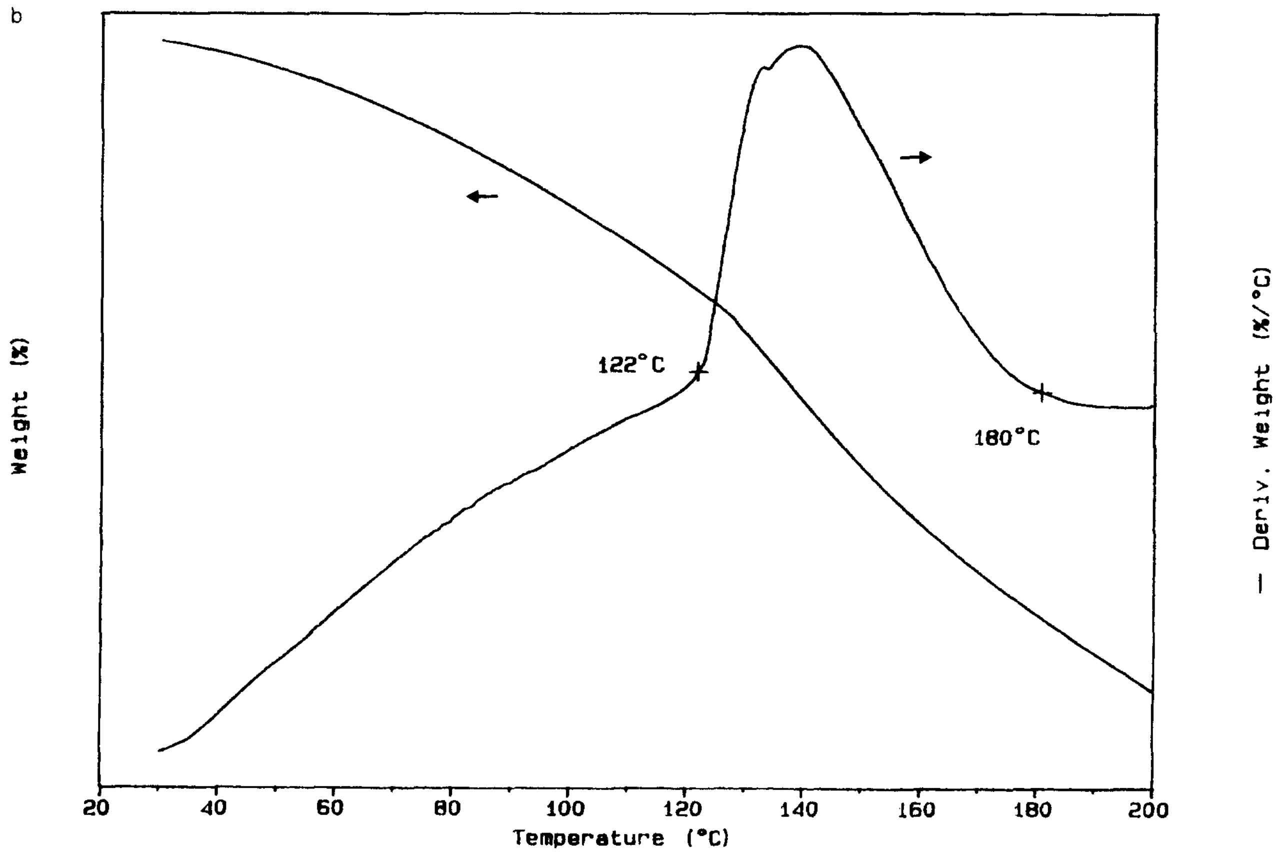


Figure 9 (a) Thermal analysis and (b) t.g.a. of TS processed in the combined twin-screw, single-screw extruders

Table 1 Morphology of TS/LDPE and TS/LLDPE blends

		Transverse				Longitudinal			
PE	C_{TS}[a] (wt%)	d_n (μm)	d_v (μm)	d_v/d_n	F	d_n (μm)	d_v (μm)	d_v/d_n	F
LDPE	8	5	16	3	1	4	16	4	0.9
LDPE	22	7	22	3	0.8	9	35	4	0.8
LDPE	36	12	103	9	0.7	18	73	6	0.5
LLDPE	7	3	7	2	0.9	3	8	3	0.8
LLDPE	39	8	27	3	0.9	8	45	6	0.9

[a] C_{TS} composition of TS in the final blend material from flow rate

Table 2 Tensile properties of TS/LDPE and TS/LLDPE blends

PE	C_{TS} (wt%)	E (MPa)	σ_y (MPa)	ϵ_y (%)	ϵ_b (%)
LDPE	0	152 (±14)	7.8 (±0.1)	58 (±1)	321 (±18)
LDPE	8	140 (±6)	7.8 (±0.1)	63 (±3)	345 (±12)
LDPE	22	109 (±7)	6.4 (±0.2)	64 (±4)	244 (±12)
LLDPE	0	223 (±25)	8.7 (±0.3)	47 (±3)	822 (±26)
LLDPE	39	136 (±7)	5.9 (±0.2)	41 (±3)	426 (±27)

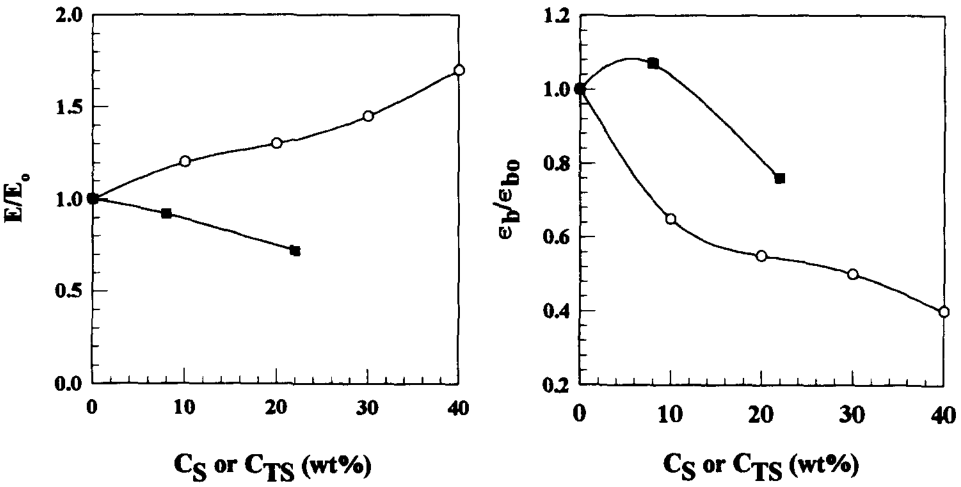


Figure 10 Relative modulus (E/E_o) and elongation at break (ϵ_b/ϵ_{bo}) of starch granules/LDPE composites[8] and TS/LDPE blends. –O– Starch granules/LDPE[8], –■– TS/LDPE

decreased to 0.7 at high TS composition in LDPE blends (*Table 1*). The shape of the dispersed phase of blends containing LLDPE was constant at $F = 0.9$ in the transverse direction. Particle–particle collisions increase with composition. Coalesced particles can contribute to elongational deformation of the dispersed phase[24]. The smaller degree of deformation observed in blends containing LLDPE resulted from a significantly smaller dispersed phase size. Smaller particles are expected to deform less than larger ones[25,26]. All these points mentioned above are, for the most part, typical characteristics of melt processed polymer blends. This supports the conclusion that the TS/PE mixture is a true polymer blend material which now has the potential for morphological control. The viscosity of LLDPE is higher than the viscosity of LDPE. The former appears to disintegrate the dispersed phase more effectively, producing a smaller and more homogeneous dispersed phase.

Tensile properties

In synthetic polymer blends, the addition of a second immiscible phase to a ductile matrix material usually significantly diminishes the elongational properties at break. In many cases when 20% of the dispersed minor phase has been added, highly deformable matrix materials are transformed into fragile materials[27]. The elongation at break, in synthetic polymer blends with a ductile matrix, is therefore considered to be highly sensitive to the state of the interface. In this study, however, high elongation at break was maintained at high loadings of starch (*Table 2*). In fact all blends containing TS and PE (LDPE or LLDPE) were highly ductile, despite the fact that no interfacial modifier was added.

The addition of starch granules results in an increased modulus and decreased elongation at break in low density polyethylene composites[3–8]. In the present study the modulus decreased as expected with addition of TS in the TS/PE blends (*Figure 10*). Even though the plasticized TS was more flexible than starch granules, the ultimate tensile stress at yield of TS/PE blends was similar to the ultimate tensile strength reported for starch composites. In the literature the ultimate tensile strength of 40% starch granules/PE composite was 70% of the ultimate tensile strength of neat polyethylene (LDPE)[8]. In this study the blends containing 22% TS in LDPE and 39% TS in LLDPE maintained high elongation even at these high loadings. Moreover, the elongation at break of TS/LDPE blends decreased less rapidly than the same properties at break reported for dry starch granule/LDPE composites[8] (*Figure 10*).

The tensile properties of starch granule/PE composites have been analysed according to well known theories for rigid particulate composites by Willett[8]. The elongation at break was found to correlate with the theoretically predicted values for systems with good adhesion even though the ultimate tensile strength correlated with systems demonstrating poor adhesion. The experimental data for elongation in that study therefore surprisingly suggested some levels of adhesion of the hydrophilic starch to the hydrophobic PE.

A mixture of TS and EVOH is the only TS/synthetic polymer blend that has been reported to demonstrate high elongational properties[14]. The vinyl alcohol provides hydroxyl groups for compatibilization with starch. The addition of EVOH (44 mol% ethylene) to TS starch plasticized with approximately 15% glycerol and 10% water improved the ductility of TS. Blends containing as much as 50 wt% TS maintained high elongational properties as observed in this study. Elongation at break of pure EVOH was found to be 325%, while the elongation of blends containing 50 wt% thermoplastic starch decreased to 300%.

As was mentioned before, the elongation at break is generally considered to be highly sensitive to the state of the interface[28]. One of the principal property modifications observed with the addition of an interfacial modifier in classical synthetic immiscible polymer blends is an increase in the elongation at break. Very high elongation at break values in what appears to be a classic immiscible system of hydrophobic PE and hydrophilic TS is the most unexpected finding of the present study. The high elongation at break was maintained even at high thermoplastic starch loadings and in the absence of an interfacial modifier.

CONCLUSION

A process to control water loss during the blending and processing of PE with TS was developed using a co-rotating twin-screw extruder with a single-screw extruder as a side feeder. This process effectively blends TS and PE in one continuous process and prevents evaporation of water before blending. TS/LDPE and TS/LLDPE were shown to have the morphology of an immiscible polymer blend with two distinct phases. The mixture displays many of the characteristics associated with a classical polymer blend such as an increase in the particle size and distribution with composition of the dispersed thermoplastic starch. These results indicate clearly that morphological control (modification of the size and the shape of the dispersed phase) can be achieved in this system. The blend material maintains very high elongational properties at break even at high loadings of TS despite the fact that the blend does not contain an interfacial modifier.

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LIST OF SYMBOLS

A	area of dispersed phase droplets
C_S	composition of starch granules (wt%)
C_{TS}	composition of thermoplastic starch (wt%)
D	screw diameter
d_n	number-average diameter
d_v	volume-average diameter
E	Young's modulus (MPa)
F	form factor
L	screw length
N	single-screw extruder screw speed
P	perimeter of dispersed phase droplets
PE	polyethylene
TS	thermoplastic starch
ϵ_b	elongation at break (%)
ϵ_{bo}	elongation at break of neat PE (%)
σ_y	ultimate tensile stress at yield (MPa)
σ_u	ultimate tensile strength (MPa)
σ_{yo}	ultimate tensile stress at yield of neat PE (MPa)
σ_{uo}	ultimate tensile strength of neat PE (MPa)

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