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Effect of moisture level on the morphology and melt flow behavior of thermoplastic starch/poly(hydroxy ester ether) blends[☆]

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Abstract

The effect of moisture content and temperature on the melt flow behavior and the resulting morphology of thermoplastic starch (TPS)/poly(hydroxy ester ether) blends is studied. The viscosity ratio (λ) was found to vary over two orders of magnitude (0.1–10) with changes in the TPS moisture content (15–30%) and temperature (120–160°C). This had a substantial effect on the level of mixing, nature of dispersion and the onset and nature of co-continuity. Deformation (in the flow direction) of the dispersed starch phase was possible under high moisture conditions (higher λ), leading to fibrillar and laminar types of morphologies at 50–80% starch level, whereas processing at a low moisture level (lower λ) produced a more dispersed morphology. When the viscosities of the two phases were significantly different, the low-viscosity polymer migrated to the surface. Surprisingly λ increased with temperature at 20% moisture TPS but decreased with temperature at 30% moisture TPS. Hence, moisture content and temperature greatly affected the surface enrichment of the lower viscosity polymer. Water partitioning took place between TPS and PHEE during extrusion, dependent on the pre-extrusion moisture content of TPS but independent of the relative concentrations of the two polymers. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Morphology; Thermoplastic starch; Viscosity ratio

1. Introduction

Starch being inexpensive, renewable and biodegradable, has been the subject of much research for thermoplastic product applications. Starch can be employed in granular form as an inexpensive filler or blended with other polymers in thermoplastic form. Blends of thermoplastic starch (TPS) with poly(ethylene-co-acrylic acid), poly(ethylene-co-vinyl alcohol) [1–4], polycaprolactone [5], poly(vinyl alcohol) [6], etc. have been studied. Biodegradable TPS blend products, under the trade names Mater-Bi® and Novon® are now also commercially available.

Starch is converted into a thermoplastic by the high pressure, high temperature and high shear extrusion conditions, in the presence of water (or other plasticizers). This process, although known for a long time, has more recently been termed destructurization (essentially gelatinization under low amounts of moisture) and leads to an almost complete destruction of the crystalline state of starch. This highly amorphous material can be remelted and re-extruded, like a thermoplastic. Extrusion parameters, such as moisture level, screw speed, temperature, and the type and amount of additives, affect the level of destructurization [7].

Hydroxy-functional thermoplastic polyesters [8] can be prepared by the reaction of diacids and diglycidyl ethers using quaternary ammonium halide salts as initiators, which apparently prevents the transesterification and cross-linking reactions [9]. These polyesters have good barrier and tensile properties [10,11] and show strong adhesion to starch [12]. Since the mechanical properties of TPS are water sensitive, there is an obvious advantage in blending TPS with PHEE. The particular polyester used in this work is derived from adipic acid and the diglycidyl ether of bisphenol A and is referred to as PHEE (poly(hydroxy ester ether)). It is an amorphous material with a glass transition temperature (T_g) of 45°C in the dry state. PHEE was

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[☆] Mention of trade names or commercial products in this article is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the US Department of Agriculture.

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shown to be readily biodegradable in a laboratory-scale compost environment [11], with approximately 98% of the polymer transformed to degradation products after 168 days of incubation.

There is limited fundamental scientific information available regarding the processing–structure–property relationships in TPS blends and it is the objective of this paper to examine some of these issues. A brief introduction to rheology–morphology relationships is provided and the relevance of this information to TPS blends is addressed. A critical role is played by moisture content in determining the rheological conditions during the blending process. The effect of varying moisture on the level of mixing, phase segregation and morphology development is examined.

1.1. Factors affecting morphology and flow-induced morphology

Immiscible blends display different types of heterogeneous morphologies, depending on the composition, viscoelastic properties of the component polymers, and the mixing process and history. In the low-composition range, one polymer is dispersed as droplets in the other polymer. As the concentration of the dispersed phase is increased, the shape of the dispersed domains may change to fiber-like (fibrillar morphology) or sheet-like (lamellar morphology). At the same time there is an increase in the continuity of the dispersed phase. Hence, an interlocked or co-continuous morphology is formed. There is, obviously, the possibility of the co-existence of the different types of morphologies. Control of the morphology is critical for tailoring the physical properties. However, it is difficult to predict the morphology due to the complexities of the processes involved during extrusion and the dynamic nature of the mixing process.

In immiscible polymer blends, rheology plays a crucial role in the development of morphology (for a comprehensive review see Refs. [13,14]). The main parameters that come into play are the viscosity ratio $\lambda = \eta_d/\eta_m$ (d is the dispersed and m the matrix phase), the interfacial tension ν and the relative elasticity of the two phases (normally measured with the first normal stress difference N_1). Many authors have observed a fine dispersion in blends where $\lambda < 1$ and a coarse one where $\lambda > 1$ [13,15,16]. Interfacial tension influences the domain size and the deformation of the dispersed phase. Increased interfacial tension increases the droplet size and it is easier to deform a larger drop than a smaller one. The relative elasticity affects the strain recovery after deformation [17,18] and hence the stability of the morphology. For λ close to 1 and $N_{1,\mathrm{d}} > N_{1,\mathrm{m}}$, strain recovery is expected and spherical droplets will result. Conversely, when $N_{1,\mathrm{d}} < N_{1,\mathrm{m}}$, strain recovery is less likely and imposed deformation can be preserved. In this case, a more fibrillar or lamellar morphology can be expected.

The mechanism of fiber formation is greatly influenced by the flow field. It is known that extensional flow field is more effective than shear in deforming disperse phase droplets [14,19]. Min et al. [20] summarized the influence of λ on deformation in the die entrance region. Uniform filaments were formed when λ was between 0.3 and 1.0, whereas spherical droplets were seen when λ was greater than 2.2. The fibrillar morphology produced in the entrance region of the capillary is subsequently lost during flow in the capillary.

Continuity of one phase in the other can occur at low volume fractions, depending on the shape of the dispersed phase [21]. Several relations give the volume fraction at which co-continuity occurs [22,23]. The simplest relationship is given by Paul and Barlow [24], as a function of viscosity ratio only:

$$\frac{\varphi_1}{\varphi_2} = \frac{\eta_1}{\eta_2} = \lambda$$

where φ and η are the volume fraction and viscosity of each phase. This expression predicts a phase inversion point, rather than a range of composition where co-continuity can exist. The interfacial tension and the elasticities can also play an important role in determining the onset of co-continuity [25]. Despite these shortcomings, this expression does show the importance of λ on the co-continuity. It also correctly predicts the tendency of the low-viscosity medium to encapsulate the higher viscosity medium.

Rheology and morphology are interdependent, since morphology generally affects the flow behavior. On the other hand, flow (for e.g. in a capillary or in the die entrance region) changes the morphology leading to flow-induced morphology [26,27]. Large differences in the viscosities of polymers generally causes increased difficulty in compounding the materials [28,29]. A very low viscosity component segregates to the high shear zones, particularly the die walls. Utracki [13] discusses the two phenomena of encapsulation during flow in a long pipe that were observed by Han [14]: (i) if $\lambda < 1$ and the normal stress ratio $\delta = N_{1,\mathrm{d}}/N_{1,\mathrm{m}} \sim 1$, the less viscous dispersed phase migrates to the wall; (ii) for systems with $\lambda \simeq 1$ but $\delta > 1$ the more elastic liquid encapsulates the lower elastic liquid. Depending on the rheological conditions, any or both of the phenomena can become important.

There are many reasons for surface segregation. The surface energy is minimized by driving the low-surface-energy component to the surface. In the case of immiscible blends, the number of energetically unfavorable contacts between unlike components can be reduced by driving the minority component towards the surface. Hence, factors such as the differences in surface tension and the interaction parameter between the components become important. Also, individual molecular weight (MW) and molecular weight distribution (MWD), and differences in MW between the components, can also play a role. Shorter chains normally tend to segregate to the surface due to lower entropy, as do stiffer chains which pack more easily [30]. Although thermodynamic factors are useful in

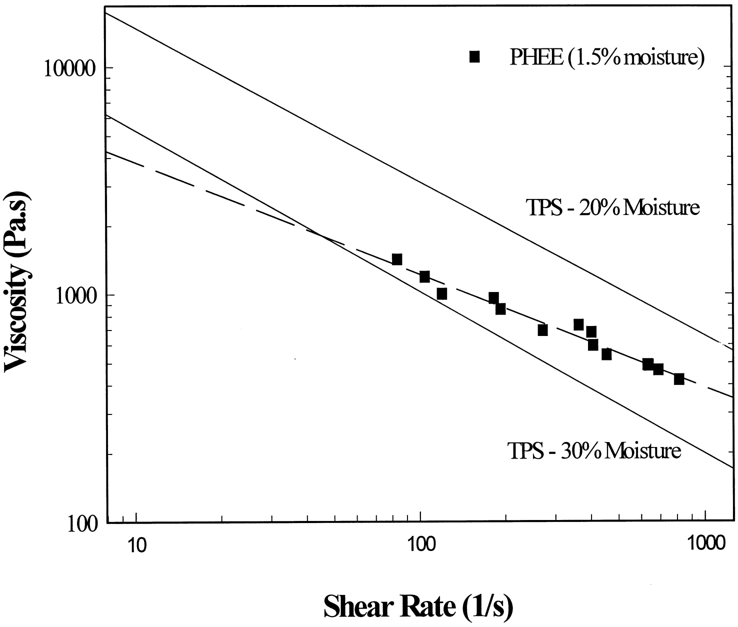

Fig. 1. Comparison of shear viscosity vs. shear rate of thermoplastic starch (20 and 30% moisture) and PHEE at 120°C.

explaining the equilibrium surface composition, kinetic factors become important where equilibrium has not been attained.

2. Experimental

2.1. Materials

The native cornstarch (~10% moisture) used in this work (Buffalo 3401) was purchased from Corn Products International, Englewood Cliffs, NJ. The cornstarch has roughly 23% by weight amylose and 77% amylopectin. PHEE was supplied by The Dow Chemical Company (Midland, MI). Cornstarch was mixed with the appropriate amount of distilled water, sealed in plastic bags and stored overnight in a refrigerator, to allow for the absorption of water. In some cases, cornstarch, PHEE and water were mixed together and stored in a similar manner prior to extrusion.

2.2. Processing and melt rheology

Extrusion was performed on a 19 mm diameter Brabender single-screw extruder (Plasticorder, Model 2000, C.W. Brabender Instruments, Inc., South Hackensack, NJ) equipped with a 30 L/D special dispersive screw. The screw has a fluted mixing section, which has been shown to be effective for starch destructurization [31]. The temperature was measured using a thermocouple in contact with the melt and the pressure using a Dynisco pressure transducer, both mounted before the capillary entrance. The 50/50 blends were first processed at 30% moisture starch (wet basis on starch), 160°C and 25 rpm, to gelatinize the starch. Films were made in the second run by extruding through a 25.4 mm slit die (0.08 mm thick). The rpm used was in the range of 20–40. Films of 50/50 blends were prepared under varying processing conditions—20 and 30% moisture and 120 and 160°C.

Rheological characterization was also made using the same screw setup as above, with a set of 2 mm capillary dies (L/D = 5, 10 and 15). Measurements on PHEE were performed at 120 and 160°C and different moisture levels. The output rate was recorded by measuring the mass of material collected (g) in 1 min intervals. A set of pressure/output rate readings was collected by varying the screw speed from 1 to 50 rpm. The data was recorded on the Brabender software, which was used to perform the Bagley end correction and the Rabinowitch correction. Shear rates of approximately 10–1000 s^{-1} were obtained.

Morphological characterization was carried out on blends that were extruded on a Leistritz 18 mm co-rotating twin screw extruder. Cornstarch powder was fed at the feed throat while water was pumped at the first zone for destructurization of starch. The extrusion was carried out with a temperature profile of 70/90/ 90/90/ 90/50°C and screw speed of 100–150 min^{-1}. The last zone was kept cool to prevent water from boiling off. Destructurized starch was pelletized and conditioned to the appropriate moisture level before blending with PHEE in the second run at 120°C and screw speed of 100–150 min^{-1}. The concentration of TPS was varied from 10 to 90% by weight and the moisture content of TPS was varied from 15 to 30%.

2.3. Analytical methods

Morphology was examined microscopically after minimally processing the samples by dry sectioning and

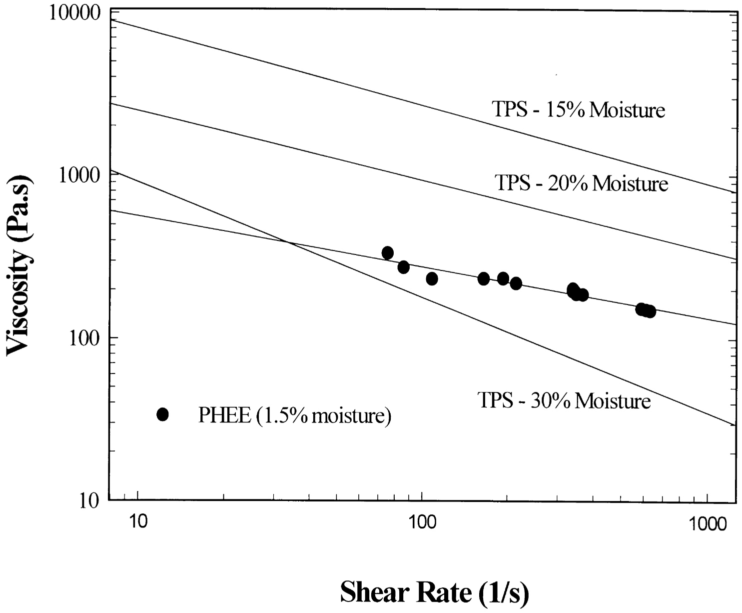

Fig. 2. Comparison of shear viscosity vs. shear rate of thermoplastic starch (15, 20 and 30% moisture) and PHEE at 160°C.

staining. Samples were embedded by immersing in paraffin wax held just above its melting point (~70°C) and allowed to cool to room temperature. Blocks were sectioned to 15 μm in various orientations using a metal knife in a rotary microtome. The sectioned samples were readily removed from the surrounding paraffin, then placed on a microscope slide and incubated overnight at room temperature in a closed container along with two separate smaller containers holding water and dry iodine crystals. Stained sections were flattened by fastening a cover glass over them, and then photographed with a Zeiss Axioskop microscope with transmitted light. Starch domains were uniformly stained reddish purple while the PHEE was light yellow. Comparison of sections cut at different orientations verified that compression or distortion of the sections was not significant.

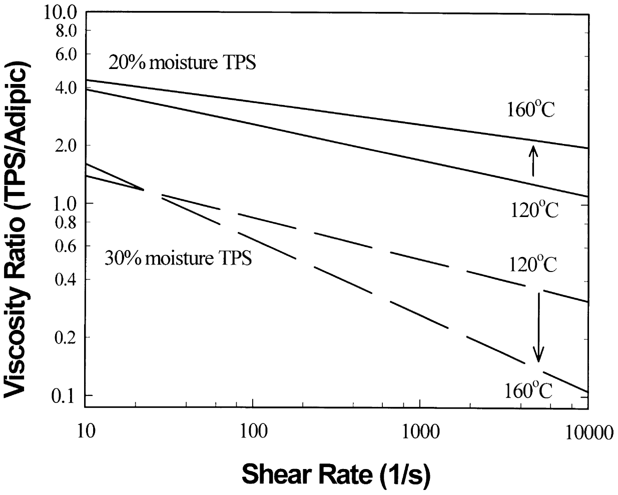

Fig. 3. Viscosity ratios of thermoplastic starch/PHEE vs. shear rates.

Differential scanning calorimetry (DSC) measurements were made on a Perkin–Elmer DSC-7 with liquid nitrogen cooling accessory. The heating scan was normally from −30 to 70°C at the rate of 10°C/min. Hermetically sealed stainless steel pans were used to minimize water loss during the scans. Moisture content was determined using an infrared detector (Ohaus model MB200, Ohaus Corporation, Florham Park, NJ) by heating at 170°C for 5 min, followed by 105°C for 15 min.

Spectra of blend films were obtained with a Matteson Polaris Fourier Transform Infrared (FTIR) spectrometer. A horizontal attenuated total reflectance (HATR) 45° zinc selenide crystal was used to obtain mid range FTIR spectra. Data was obtained for 160 scans and the spectrum was limited to 700–4000 cm^{-1}.

3. Results and discussion

Melt viscosity of cornstarch as a function of moisture and temperature has already been characterized in our research laboratory by Willett et al. [32], using the same cornstarch and the same equipment as in the present study. The viscosities of TPS (taken from Ref. [32]) and PHEE (~1.5% moisture under ambient conditions) at 120 and 160°C are shown in Figs. 1 and 2, respectively. At both 120 and 160°C, the viscosity of PHEE is intermediate between that of 20 and 30% moisture TPS with a crossover point at around 30–50 s^{-1} with 30% TPS. Hence, the viscosity of TPS can be greater or less than that of PHEE, depending on the shear rate. This is as a result of the difference in the power law index (slope of the viscosity vs. shear rate plot) of the two polymers.

The viscosity ratio (λ), defined as the viscosity of TPS

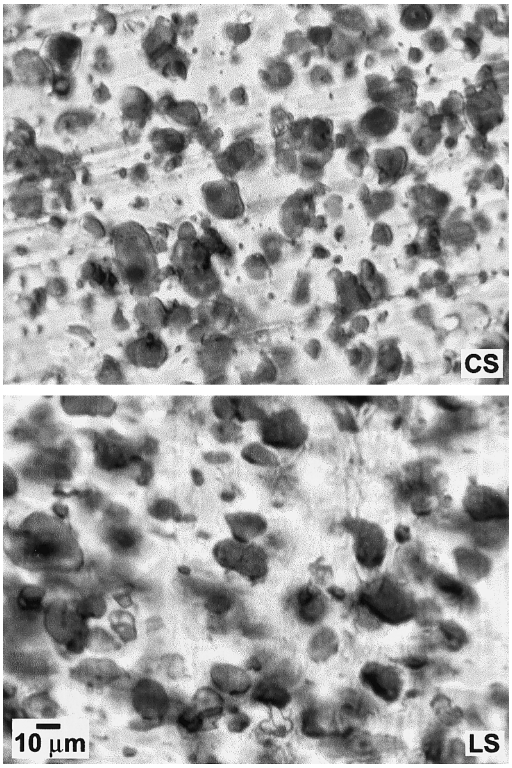

Fig. 4. Optical micrograph showing cross- and longitudinal section views of a 40/60 TPS/PHEE blend, processed at 25% moisture starch.

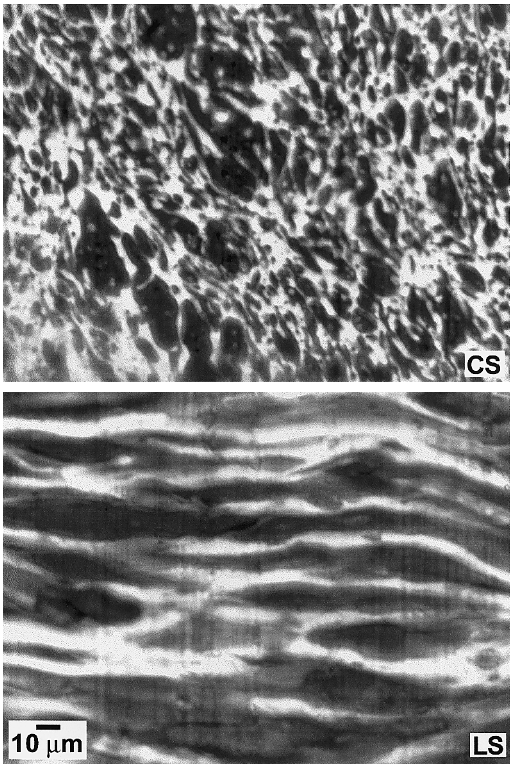

Fig. 5. Optical micrograph showing cross- and longitudinal section views of a 50/50 TPS/PHEE blend, processed at 25% moisture starch.

over PHEE, is plotted as a function of shear rate in Fig. 3. The calculation of the viscosity ratio was based on the regression lines for the viscosity data for TPS and PHEE. At 120°C and for 20% moisture TPS, λ has a fairly high value of 2–4, in the shear rate range of 10–1000 s^{-1}. The corresponding range of λ is 0.5–1.5 for 30% moisture TPS at 120°C. At 160°C, the ratio could be close to 10 for 15% moisture TPS and 0.1 for the 30% moisture TPS blends. Hence, there is a two order of magnitude change in λ with only a 15% change in moisture level. These results clearly show the wide range of λ's that could be encountered in the often used moisture levels of 15–30% for TPS extrusion.

3.1. Effect of viscosity ratio on morphology

The effect of λ on the morphology of the blends was examined by varying the moisture level of the starch phase at a constant temperature of 120°C. Three series of blends (with varying concentrations) were prepared on the Leistritz co-rotating twin screw extruder at TPS moisture contents (mc) of 16, 19 and 25%. The preparation of the blends was a two-step process, where starch was destructurized in the first step by extrusion at 120°C and 30% moisture. SEM pictures showed the absence of starch granules and X-ray diffraction patterns showed complete loss of crystallinity. TPS was then conditioned to the desired moisture level and blended with PHEE at 120°C. Optical pictures were taken in the cross-section (CS) and longitudinal section (LS) of the extruded samples which had been stained with iodine vapor.

At the 25% TPS moisture level, starch was the dispersed phase in the 10–40% concentration level. The morphology was the same in the CS and LS, indicating no deformation in the flow direction (Fig. 4). The starch particles (visible as the darker phase) are typically 1–20 μm but some particles greater than 200 μm are also present. At the 50% starch level, however, significant deformation in the flow direction was visible (Fig. 5). The shape of the starch domains was round to ellipsoidal (~10 μm) in the CS but highly elongated (200–400 μm) in the LS, indicating a fibrillar morphology. It is apparent that the deformation of the starch domains is accompanied with coalescence since no deformation was visible at the 40% starch level. Composite drops of PHEE and TPS can be seen in the CS, indicating the onset of some level of continuity of the starch phase. At the 60% starch level (Fig. 6), the CS shows longer starch domains, whereas the LS still shows highly elongated domains. Hence, there is the presence of both fibrillar and laminar morphologies. There is also an increased presence of composite drops in the CS. In the LS, the distinction between the dispersed and continuous phase has disappeared. This indicates a greater degree of co-continuity of the two phases. At the 70 and 80% starch levels, the two phases are co-continuous.

At the 16% TPS moisture level, there is a noticeable

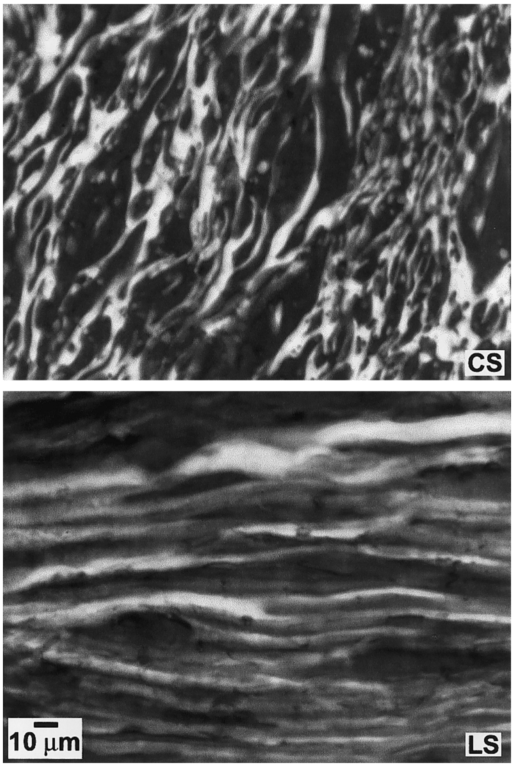

Fig. 6. Optical micrograph showing cross- and longitudinal section views of a 60/40 TPS/PHEE blend, processed at 25% moisture starch.

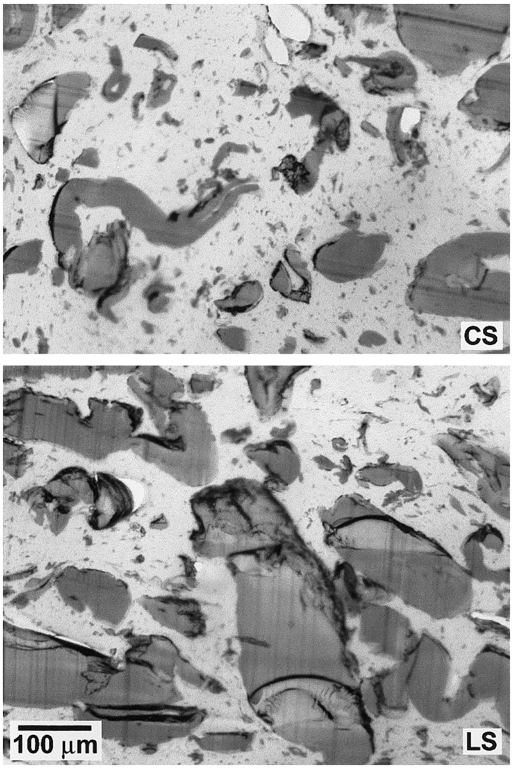

Fig. 8. Optical micrograph showing cross- and longitudinal section views of a 40/60 TPS/PHEE blend, processed at 16% moisture starch.

change in the morphology, especially at the higher starch concentrations. Fig. 7 shows the overall CS view of 10% starch blends processed at 16 and 25% mc TPS. Some wax, which was used as the embedding medium, can be seen at the periphery of the samples. It can clearly be seen that there is much lower dispersive mixing at the 16% mc TPS, where most of the starch is in the form of a few large sized domains. From Fig. 3, it can be seen, on extrapolation, that at high shear rates, λ is in the range of 4–6 for 16% mc TPS and 1–2 for 25% mc TPS. Breakup of the disperse phase droplets is more difficult at the higher viscosity ratio. These large sized irregular shaped particles could also

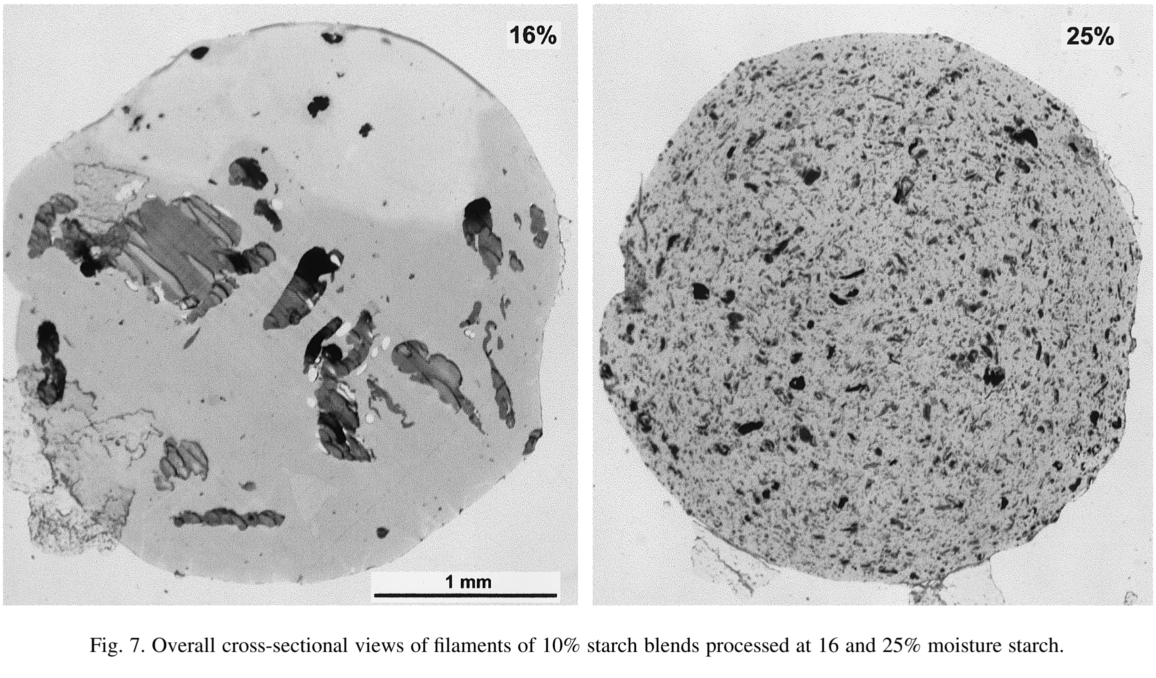

Fig. 7. Overall cross-sectional views of filaments of 10% starch blends processed at 16 and 25% moisture starch.

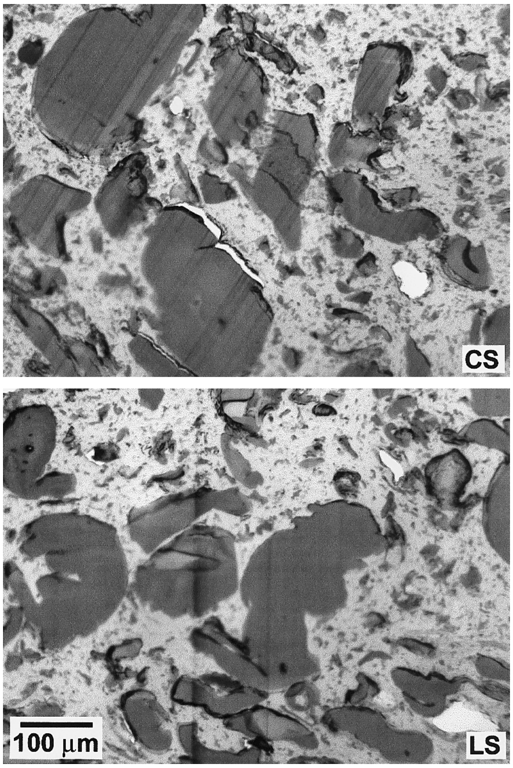

Fig. 9. Optical micrograph showing cross- and longitudinal section views of a 50/50 TPS/PHEE blend, processed at 16% moisture starch.

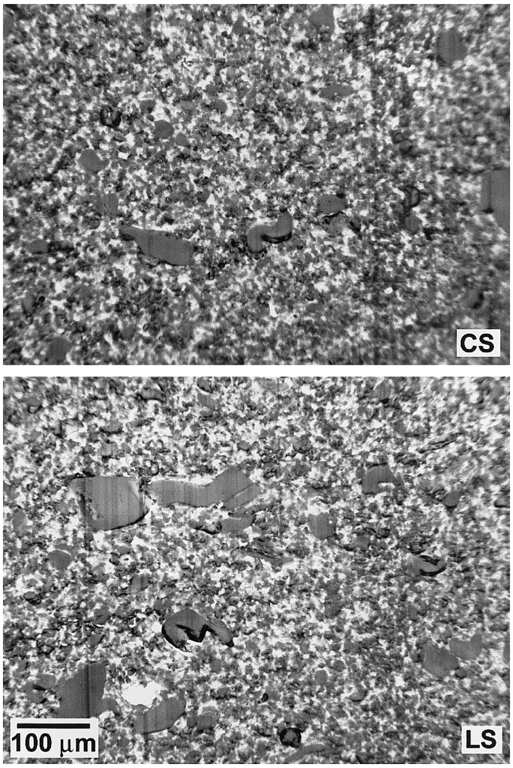

Fig. 10. Optical micrograph showing cross- and longitudinal section views of a 60/40 TPS/PHEE blend, processed at 16% moisture starch.

possibly be remnant swollen starch granules. Fig. 8 shows the 40% starch blend at the starch moisture level of 16%. Two different sized particles are present, some of which are 10 μm or less and others which are well above 200 μm. However, there is a higher number of these large sized particles at the 16% mc, as compared with 25% mc TPS.

Fig. 9 shows the 50% starch blend for the case of 16% mc TPS. The CS and LS views are the same, with starch clearly the dispersed phase. No longitudinal deformation of the dispersed phase can be seen at the 16% mc TPS, in contrast to the 25% mc TPS. The high λ, apparently, impedes the formation (or preservation) of fibrillar morphology in the die entrance region. Also at the 25% mc TPS blends, there was onset of continuity of the starch phase at the 50% level, whereas with the 16% mc TPS blends, starch is still clearly dispersed. It would then appear that the high λ shifts the onset of co-continuity to higher disperse phase concentrations. The shape of the dispersed phase plays a critical role [21] since the percolation threshold value for fibers (or elongated structures) is lower than spherical particles.

Fig. 10 shows the 60% blend for 16% mc TPS. Continuity of the starch phase is apparent at this (and higher) concentrations. It can also be seen that the CS and LS views are identical, showing lack of deformation in the flow direction, even at very high starch concentrations. There was a significant increase in the extrusion pressure on going from 50 to 60% starch level. It is possible that the onset of continuity of the starch phase increases the shear stresses due to the much higher viscosity of the starch phase. In fact, blends higher than 70% starch could not be extruded because the pressures exceeded the extruder limits. No such increase in pressures were observed with an increase in starch concentration for the case of 25% mc TPS blends, where viscosity of starch was comparable to that of PHEE.

The compositional influence on the morphology of TPS/PHEE blends is very similar to that reported for blends of TPS with other polymers [33,34]. Simmons et al. [33] observed starch domain sizes of 0.1–4 μm for starch concentrations up to 50% by weight in starch/poly(ethylene-co-vinyl alcohol)(EVOH) blends. There was a dramatic increase in domain sizes from 50 to 75% by weight of starch. Some miscibility between starch and EVOH was observed and that could explain the finer morphology observed in that case. Also the shear stresses present during processing could be different. However, EVOH was observed to be the continuous phase up to starch concentrations of 70%.

3.2. Effect of viscosity ratio on phase migration

An interesting observation was the presence of higher than expected amounts of PHEE on the surface of the extruded films and strands under some processing conditions. In some instances, PHEE could be seen to collect at the die lip and would periodically discharge on the extrudate as rings. Attenuated total reflectance FTIR spectroscopy

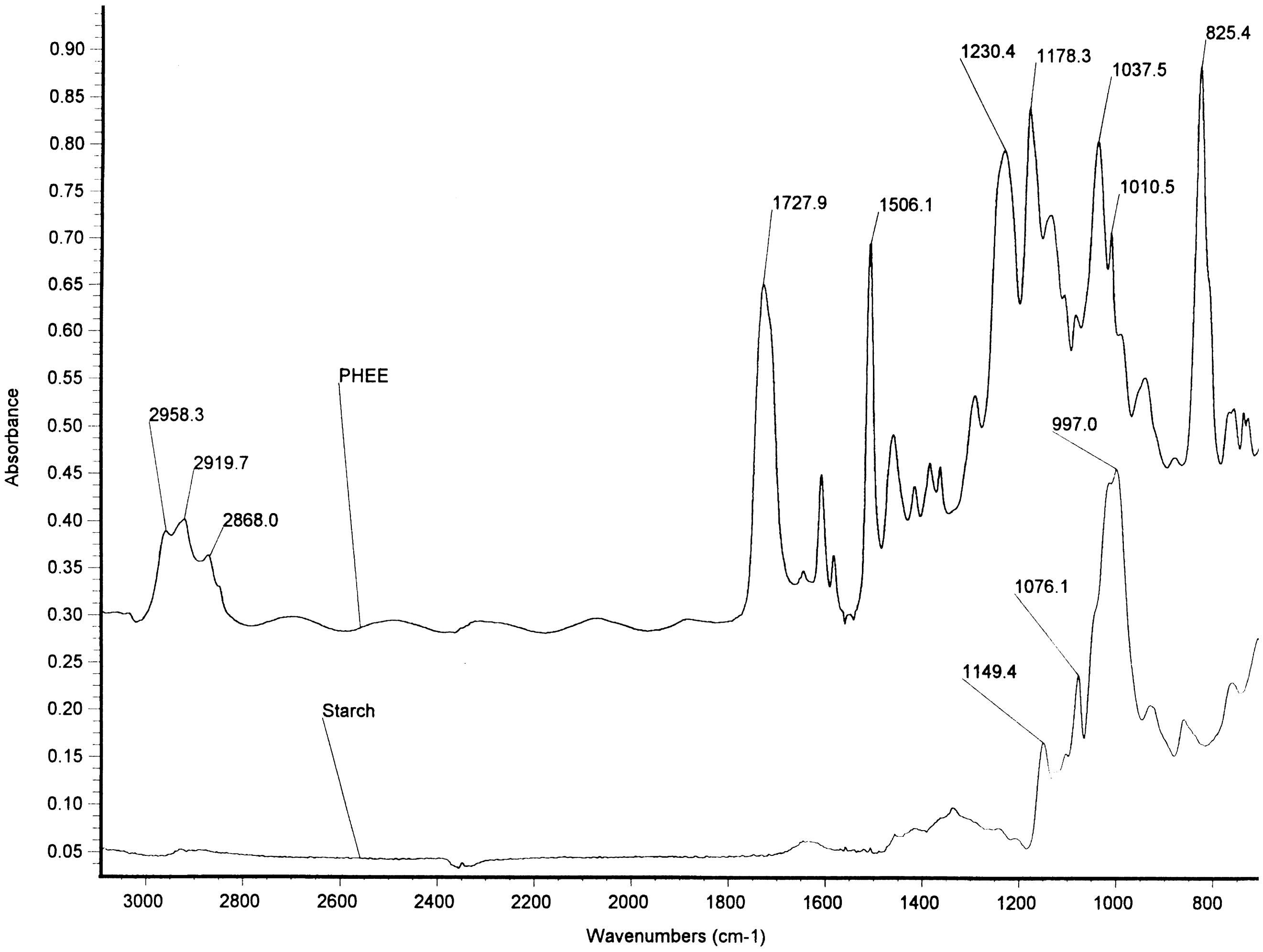

Fig. 11. Attenuated total reflectance FTIR spectra of thermoplastic starch and PHEE.

technique was used to explore this phenomenon. This technique analyzes the surface of a specimen in the 0.5–3 μm range. The depth of penetration strongly depends on the wavelength of incident light, which makes exact quantitative interpretation difficult. ATR is also very sensitive to the surface contact of the film since the calculated depth of penetration includes the air gap between the crystal and the sample. For this reason, only a comparison of the relative intensity of peaks uniquely associated with starch and PHEE was attempted. Fig. 11 shows the spectra for pure starch and PHEE resin. The only unique peak for starch lies at around 990 cm^{-1}, although PHEE shows some absorbance at that wavenumber. PHEE shows prominent peaks at roughly 1728, 1507, 1230 and 825 cm^{1}. The 1230 cm^{-1} peak would be affected by the presence of starch and the 1507 cm^{-1} peak would have problems with the baseline. The valleys on either side of the 825 cm^{-1} peak are partially filled by the starch peak. From this aspect, it would be preferable to use the 1728 cm^{-1} peak. The main reason for wanting to use the PHEE 825 cm^{-1} peak is its proximity to the starch 990 cm^{-1} peak and farther apart the peaks are, the more sensitive the ratio will be to air gap effects. Since it is not clear whether the 1728 or 825 cm^{-1} peak would be more useful, both the peaks are used. The ratio of peak absorbance at 990 to that of 1728 (or 825) cm^{-1} is

Table 1
Relative proportion of TPS/PHEE as defined by peak absorbance ratios for the different 50/50 blend samples

50/50 Blend	Ratio 1 (990/1728)	Ratio 2 (990/825)	Viscosity ratio (λ)
20% mc TPS, 120°C	1.06	0.91	1.77
20% mc TPS, 160°C	0.24	0.20	2.65
30% mc TPS, 120°C	1.39	1.10	0.54
30% mc TPS, 160°C	7.16	13.3	0.28

taken as an indication of the relative proportion of starch and PHEE on the film surface.

The 50/50 blend films processed under different conditions were analyzed. The spectra for the 20% mc TPS blend looks similar to that for pure PHEE at 160°C, in contrast to that at 120°C, suggesting significant migration of PHEE to the surface on increasing the temperature. On the other hand, at 30% moisture, an increase in temperature leads to a decrease in surface concentration of PHEE or an increased migration of TPS to the surface. To quantify the above observations, the two absorbance ratios (990/1728 and 990/825) for the different samples are shown in Table 1. It is clear that both the ratios predict the same trend on increasing the temperature from 120 to 160°C—increase in starch proportion at 20% TPS moisture and decrease at the 30% TPS moisture level. From these results, it appears that either PHEE peak could be used to indicate relative starch/PHEE proportion.

To better understand the above effect, the viscosity ratios should be looked at as a function of temperature. Fig. 3 clearly shows that there is an increase in λ as temperature is increased for the 20% moisture TPS, the effect being larger at higher shear rates. The ratio is always greater than 1 or that viscosity of PHEE is always lower than TPS. This would suggest that at 160°C, the difference in viscosity of PHEE and TPS is larger and this results in more migration of the low-viscosity PHEE to the surface. On the other hand, Fig. 3 also shows that the ratio is less than 1 for 30% moisture TPS or that the viscosity of TPS is always lower than that of PHEE. Surprisingly, λ decreases on increasing the temperature, in contrast to the 20% moisture case. Hence at 160°C, the difference in viscosity of TPS and PHEE would be greater. Interestingly, the above results indicate that there is possibly a moisture content between 20 and 30% where λ will be insensitive to temperature. It is clear that the lower viscosity phase shows a higher surface concentration at 160°C, irrespective of the moisture content. Table 1 also shows the corresponding λ's, calculated at an estimated shear rate of 800 s^{-1} in the slit die (based on the volumetric flow rate and dimensions of the slit die). The absorbance ratio increases as the viscosity ratio decreases.

Utracki et al. [35] observed a similar effect of temperature on high-density polyethylene (HDPE)/polyamide (PA) blends. At 150°C, more HDPE was present on the surface, while the situation was reversed at 250°C. In either case, it was the low-viscosity phase which was migrating to the high stress region at the walls. These observations can be explained by the “principle of energy minimization,” whereby the presence of the low-viscosity medium in the high-stress region minimizes the energy dissipation of the system. The rate of migration would be dependent on parameters such as stress gradient (which could cause differences in slit and round capillaries), λ and δ. The residence time would also play an important role in determining the extent of migration. Another factor to bear in mind is that λ will change with radial position, since shear stress varies from a maximum at the wall to zero in the center. This can lead to differences in the driving force for shear segregation along the radius. Uneven radial distribution of moisture can further complicate the situation. Thermal and shear degradation of starch during extrusion will change the MW and MWD, and this would be affected by moisture content and extrusion temperature. In a two-pass extrusion of starch, it has been shown that thermal effects are more important than shear effects in the second pass [7].

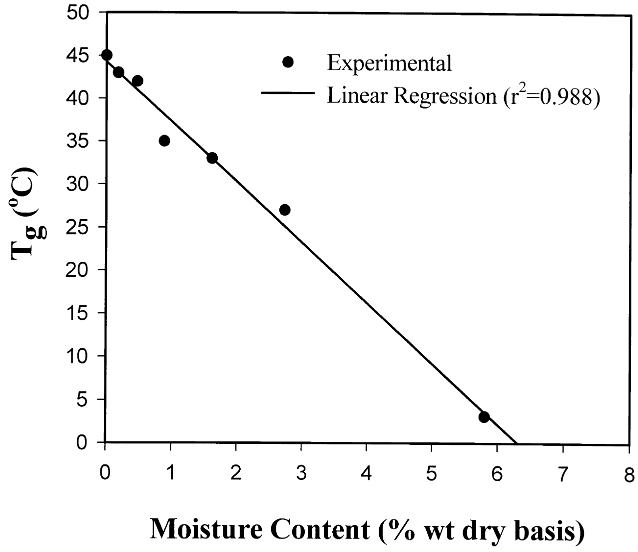

Fig. 12. Plot of glass transition temperature vs. moisture content of PHEE.

From an application standpoint, it would be desirable to have a hydrophobic coating to improve the moisture resistance of these products. Such a migration was also observed by Simmons et al. [2,33] for the case of TPS/EVOH blends. In their work, EVOH was found to coat the surfaces of filaments, even at as high as 70% starch levels. The surface structure was confirmed by enzymatic etching of the fibers and observation in the SEM. The surface enrichment of EVOH was attributed to the lower viscosity of EVOH.

3.3. Effect of PHEE moisture level

The glass transition temperature (T_g) of PHEE changes from 45°C in the dry state to 5°C at 6% moisture level (Fig. 12). In fact, the relationship of T_g with moisture content is linear ($r^2 = 0.988$). There is a plasticizing effect of water on the viscosity of PHEE, which decreases with increasing moisture level. PHEE is fairly hydrophobic and only reaches an equilibrium moisture level of close to 6% under 100% humidity conditions. When wet TPS (15–30% moisture) is extruded with ambient PHEE (~1.5% moisture), there is the possibility of water partitioning between TPS and PHEE. Such a moisture redistribution would affect the viscosities of the two phases and hence λ. However, the actual effect of water partitioning on the morphology of the blend would depend on the relative kinetics of moisture partitioning and the blending process.

Table 2
Moisture content of thermoplastic starch after extrusion (based on a PHEE moisture content of 4.4% in the extruded blends; moisture content of thermoplastic starch before extrusion = 25%)

% TPS/PHEE	MC starch(%)	T_g PHEE (°C)
20/80	16.7	14.7
40/60	22.1	14.2
50/50	23.1	13.9
60/40	23.7	13.2
70/30	24.2	12.9
80/20	24.5	12.8

It should be pointed out that the viscosity ratios reported in this work are based on the initial moisture content and have not been corrected for the above-mentioned moisture partitioning.

It is difficult to measure the moisture content of each phase in the extruded blends. Hence, the approach used here was to measure the T_g of the PHEE phase and calculate the moisture content, using the data for the pure material (Fig. 12). Knowing the blend moisture content, the amount of water remaining in the starch phase can then be calculated. The above analysis was carried out on a series of blends of different concentration that were processed on the Leistritz TSE at 120°C and 100–150 min^{-1}. Ambient PHEE and TPS at 25% moisture were used to prepare the blends. The T_g of PHEE was measured in the as-extruded sample and was very reproducible in two consecutive DSC heating runs, suggesting no loss or redistribution of moisture in the first heating run. Also the T_g of PHEE in the blend increases to 45°C on drying the sample, confirming that the change was due to increased moisture level and not any possible interaction between starch and PHEE. The T_g values for the different concentration blends are listed in Table 2. Surprisingly, the values are essentially the same, irrespective of the amount of starch present. A T_g of ~13.5°C corresponds to a moisture content of 4.4% in the PHEE phase. Hence, during processing, PHEE picks up moisture from the starch phase. The moisture level of starch would decrease during processing, the amount being dependent on the proportion of starch present. Therefore, as water transfer takes place during extrusion, the viscosity of the starch phase would increase and that of PHEE decrease, causing an increase in λ. Table 2 shows the moisture level in TPS after extrusion, and the value ranges from 16.7 to 24.5% as starch content changes from 20 to 80% by weight. From a rheological standpoint, the mixing conditions are not the same at each concentration.

Blends were also prepared at two other moisture levels of TPS—16 and 19%. As before, the T_g values of the different concentration blends at each moisture level were essentially the same. The T_g values of PHEE were roughly 18.5°C at the 19% mc and 22.0°C at the 16% mc, corresponding to a PHEE moisture level of 3.7 and 3.2, respectively. Hence, as the moisture content of TPS before extrusion is decreased, so does the final level of moisture of PHEE in the extruded blend, there being an almost apparent linear relationship between the two variables (Fig. 13).

Although not investigated in this work, there are other possible factors that can affect the partitioning of moisture. Does the redistribution change as a function of processing temperature, shear rate, residence time, and rpm (which would change the shear rate and residence time)? Also does the processing equipment or the screw configuration affect this process? Preliminary results indicate that processing of the blends on the Brabender single screw extruder and ZSK-30 twin screw extruder showed similar results.

4. Conclusions

The importance of moisture content of TPS during extrusion has clearly been demonstrated, as well as the water partitioning between TPS and PHEE. These factors directly affect the viscosity ratios encountered during processing.

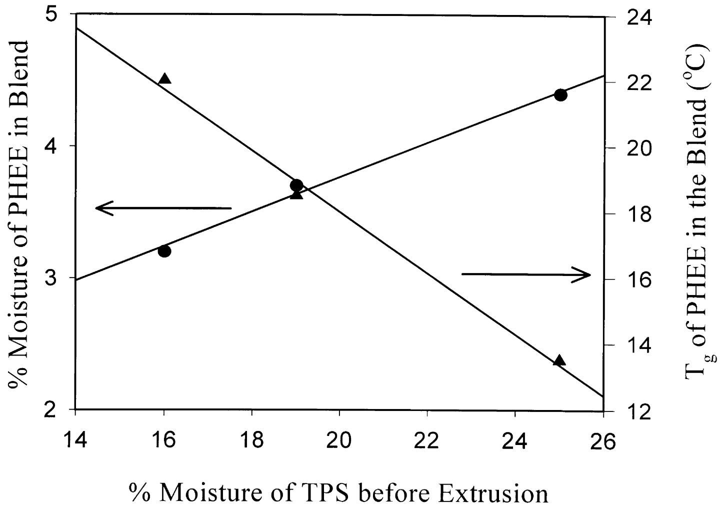

Fig. 13. Relationship between the moisture content of PHEE in the extruded blend to the moisture content of TPS before extrusion.

The wide range of possible values for λ has an influence on the size of dispersion, type of morphologies developed and the onset and nature of continuity of the starch phase. Hence, it is important to control the moisture (or plasticizer) level and temperature used during processing, as this can greatly influence the final blend properties (this will be addressed in a future publication). On the other hand, varying moisture could be an easy method by which the morphology and properties could be tailored.

Starch is composed of two very high molecular weights components—fairly linear amylose (10^5–10^6) and highly branched amylopectin (10^7–10^9). Hence, it is to be expected that TPS is a highly elastic material and that differences in elasticity between TPS and the other polymer could exist. Due to the high MW's, high interfacial tensions are expected in TPS blends. It is possible that both interfacial tension and elasticity can vary as a function of moisture content, especially since the presence of water can affect the level of hydrogen bonding between the starch molecules and also possibly between starch and the other polymer. Further, significant shear and thermal degradation takes place during processing of TPS, which can change the MW and MWD. This would affect the viscosity, elasticity and the interfacial tensions. Although the scope of this investigation was preliminary, the importance of these rheological factors can clearly be imagined.

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References

[1] George ER, Sullivan TM, Park EH. Polym Engng Sci 1994;34:17.
[2] Simmons S, Thomas EL. J Appl Polym Sci 1995;58:2259.
[3] Villar MA, Thomas EL, Armstrong RC. Polymer 1998;36:1869.
[4] Stenhouse PJ, Ratto JA, Schneider NS. J Appl Polym Sci 1997;64:2613.
[5] Bastioli C, Cerutti A, Guanella I, Romano GC, Tosin M. J Environ Polym Degrad 1995;3:81.
[6] Park EH, George ER, Muldoon MA, Flammino A. Polymer News 1994;19:230.
[7] Willett JL. Woodfiber–Plastic Composites (Proceedings)—Virgin and Recycled Wood Fiber and Polymers for Composites, 1996. p. 100.
[8] Mang MN, White JE. US Patent, 5,171,820, 1992.
[9] Mang MN, White JE, Haag AP, Kram SL, Brown CN. Papers presented at the Chicago, Illinois Meeting of American Chemical Society 1995;36:180.
[10] Mang MN, White JE, Kram SL, Bailey RE, Swanson PE. Proc ACS Div Polym Mater: Sci Engng 1997;76:412.
[11] Rick DL, Davis JW, Lickly TD, Mang MN. Sixth Annual Meeting of the Bio/Environmentally Degradable Polymer Society, San Diego, September 17–20, 1997.
[12] Willett JL. Polym Prepr Div Polym Chem, ACS Proc Boston Meeting 1998;39:112.
[13] Utracki LA. Polymer alloys and blends—thermodynamics and rheology. New York: Hanser, 1989.
[14] Han CD. Multiphase flow in polymer processing. New York: Academic Press, 1981.
[15] Favis BD, Chalifoux JP. Polym Engng Sci 1987;27:1591.
[16] Wu S. Polym Engng Sci 1987;27:335.
[17] Elmendorp JJ. Polym Engng Sci 1986;26:418.
[18] Vanoene H. J Coll Inter Sci 1972;40:448.
[19] Gonzalez-Nunez R, Favis BD, Carreau PJ, Lavallee C. Polym Engng Sci 1993;33:851.
[20] Min K, White JL, Fellers JF. Polym Engng Sci 1984;24:1327.
[21] Willemse RC, Posthuma De Boer AP, Van Dam J, Gotsis AD. Polymer 1998;39:5879.
[22] Lyngaae-Jørgensen J, Utracki LA. Makromol Chem Macromol Symp 1991;48/49:189.
[23] Utracki LA. J Rheol 1991;35:1615.
[24] Paul DR, Barlow JW. J Macromol Sci, Rev Macromol Chem 1980;C18:109.
[25] Favis BD, Bourry D. J Polym Sci Part B: Polym Phys 1998;36:1889.
[26] Utracki LA, editor. Two-phase polymer systems New York: Hanser, 1991 (chap. 1).
[27] White JL, Min K. Makromol Chem Macromol Symp 1998;16:19.
[28] Scott CE, Joung SK. Polym Engng Sci 1996;36:1666.
[29] Grace HP. Chem Engng Commun 1982;14:225.
[30] Schmid F. J Chem Phys 1996;104:9191.
[31] Willett JL, Jasberg BK. Proc ACS Div Polym Mater Sci Engng 1995;72:183.
[32] Willett JL, Jasberg BK, Swanson CL. Polym Engng Sci 1995;35:202.
[33] Simmons S, Thomas EL. Polymer 1998;39:5587.
[34] St-Pierre N, Favis BD, Ramsay BA, Ramsay JA, Verhoogt H. Polymer 1997;38:647.
[35] Utracki LA, Dumoulin MM, Toma P. Polym Engng Sci 1986;26:34.