Polymer 44 (2003) 1517–1526

polymer

www.elsevier.com/locate/polymer

High performance LDPE/thermoplastic starch blends: a sustainable alternative to pure polyethylene

F.J. Rodriguez-Gonzalez[1], B.A. Ramsay[2], B.D. Favis*

Department of Chemical Engineering, Centre de Recherche Appliquée Sur les Polymères (CRASP), École Polytechnique de Montréal,
P.O. Box 6079, Succursale Centre-ville, Montréal, Qué., Canada H3C 3A7

Received 8 July 2002; received in revised form 25 November 2002; accepted 27 November 2002

Abstract

Thermoplastic starch (TPS), as opposed to dry starch, is capable of flow and hence when mixed with other synthetic polymers can behave in a manner similar to conventional polymer–polymer blends. This paper presents an approach to preparing polyethylene/thermoplastic starch blends with unique properties. A one-step combined twin-screw/single screw extrusion setup is used to carry out the melt–melt mixing of the components. Glycerol is used as the starch plasticizer and its content in the TPS is varied from 29 to 40%.

Under the particular one-step processing conditions used it is possible to develop continuous TPS (highly interconnected) and co-continuous polymer/TPS blend extruded ribbon which possess a high elongation at break, modulus and strength in the machine direction. The PE/TPS (55:45) blend prepared with TPS containing 36% glycerol maintains 94% of the elongation at break and 76% of the modulus of polyethylene. At a composition level of 71:29 PE/TPS for the same glycerol content, the blend retains 96% of the elongation at break and 100% of the modulus of polyethylene. These excellent properties are achieved in the absence of any interfacial modifier and despite the high levels of immiscibility in the polar–nonpolar TPS–PE system. The 55:45 blend possesses a 100% continuous or fully interconnected TPS morphology, as measured by hydrolytic extraction. This highly continuous TPS configuration within the blend should enhance its potential for environmental biodegradation. The elongation at break in the cross direction of these materials, although lower than the machine direction properties, also demonstrates ductility at high TPS concentrations. At a glycerol content of 36% in the TPS, the blends demonstrate only very low levels of sensitivity to moisture. A high degree of transparency is maintained over the entire concentration range due to the similar refractive indices of PE and TPS and the virtual absence of interfacial microvoiding.

Effective control of the glycerol content, TPS concentration and processing conditions can result in a wide variety of morphological structures including spherical, fiber-like, highly continuous and co-continuous morphologies. These various blend morphologies are shown to be the determining parameters with respect to the observed mechanical properties.

This material has the added benefit of containing large quantities of a renewable resource and hence represents a more sustainable alternative to pure synthetic polymers.

Keywords: Thermoplastic Starch; Polymer Blends; Morphology; Properties

---

1. Introduction

Starch is a natural carbohydrate storage material accumulated by green plants in the form of granules. It is composed of linear polysaccharide molecules (amylose) and branched molecules (amylopectin) and is an inexpensive, renewable and natural polymer. It can be added to synthetic polymers to lower the cost of the final product. Numerous studies have shown that the addition of dry starch granules to low density polyethylene (LDPE) follows the general trend for filler effects on polymer properties [1,2]. The modulus increases due to the stiffening effect of the starch granules and the elongation decreases as the starch content is increased. In pioneering work, Griffith [3] reported on the preparation of starch-filled polyethylene (PE) composites. Ductile films could be prepared at low starch loading, but the films became paper-like when starch content exceeded 15% [3]. In a fashion typical of that observed for mineral fillers, the addition of granular starch to PE results in a severe reduction of tensile strength ($\sigma_{\max}$) and elongation at

---

* Corresponding author. Tel.: +1-514-340-4818; fax: +1-514-340-4159. *E-mail address:* basil.favis@polymtl.ca (B.D. Favis).

[1] Centro de Investigación en Química Aplicada, Saltillo, México 25100.

[2] Polyferm Canada, RR#1, Harrowsmith, Ont., Canada K0H 1V0.

0032-3861/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(02)00907-2

break (ε_b), while the elastic modulus (E) increases [2,4,5]. Some improvement of σ_{max} and E can be achieved through modification of the non-polar polyolefin and the polar granular starch interface [2,5].

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 and the crystallinity is progressively destroyed. This process is called gelatinization [6]. The processing of starch and water in a heated extruder is an efficient way to obtain gelatinized starch (GS) since the high shear that can be generated in the extruder disrupts the starch granules.

Extensive work has been devoted to the development of materials containing GS. Otey et al. developed GS/EAA cast films that demonstrated good transparency, flexibility and mechanical properties [7,8]. Blends of GS with other polymers were prepared by first mixing starch, ethylene–acrylic acid copolymer (EAA) and other additives in a long initial process. The resultant dough was then extruded several times to improve the homogeneity and to reduce the moisture content to the desired value. Blown films of these GS/EAA blends, compounded with LDPE and polyvinyl alcohol (PVA), were extruded in a further step. The addition of LDPE led to the reduction of both σ_{max} and ε_b. Incorporation of PVA increased the ε_b of starch-based films. Otey's process was improved [9] and modified by other authors [10,11]. The use of the original formulation or a slight modification thereof was a characteristic of the subsequent works. Detailed studies on this polymeric system were devoted to the fundamental understanding of the interactions between starch components and EAA. Solvent extraction [12], X-ray diffraction [12,13], CP/MAS, solid state NMR [13], FTIR [13], optical rotation [14], bacterial degradation [15], fluorescence microscopy [15] and DSC [15] were used to study the complexation reaction of amylose and amylopectin with EAA. Those works demonstrated that amylose and amylopectin form V-type inclusion complexes with EAA. The hydrophobic segment of EAA molecules is trapped in the hydrophobic core of the starch helix. Amylose/EAA complexes are highly crystalline and resistant to enzymatic attack. Conversely, amylopectin/EAA complexes are poorly crystalline and are susceptible to amylolytic attack. These findings led to the proposal that compatibilizers other than EAA should be employed to improve interfacial adhesion with PE and reduce the GS particle size, without promoting the formation of starch complexes [15].

Addition of a plasticizer such as glycerol can further improve the ductility of GS. Plasticized GS is known as thermoplastic starch (TPS) and is capable of flow. Thus, mixtures of TPS with other polymers have the potential to behave in a manner similar to conventional polymer–polymer blends. The melt blending of TPS has been studied with polyethylene [16–22] and biodegradable polyesters such as polycaprolactone [23–25], polyesteramide [24–26], polylactic acid [25,27], poly(butylene adipate-*co*-terephtalate) [25,26], poly(butylene succinate adipate [25,26] and poly(hydroxy ester ether) [28,29]. The tensile properties of these blends decreased significantly as TPS content increased. The elongation at break is the property most adversely affected by the presence of TPS particles and typically ductile polymers, such as polyethylene and polycaprolactone, became fragile with the addition of 20–30 wt% TPS.

TPS/polyolefin blends have not been frequently studied since the general bias in the literature is that the two materials are too dissimilar and none of the above papers have attempted to systematically control the TPS morphology. St-Pierre and coworkers [18] reported on a one-step blending process for TPS/polyethylene blends. They developed an extrusion system combining a twin-screw extruder (TSE) with a single-screw extruder (SSE). TPS was prepared in the SSE, and then it was blended with LDPE in the final sections of the TSE. The LDPE/TPS morphology displayed the typical characteristics of immiscible polymer blends where the particle size increased as the TPS content increased. The mechanical properties showed a small reduction in the Young's Modulus and strength at yield with TPS concentration. On the other hand, the elongation at break dropped dramatically at TPS contents greater than 10%. The highest TPS loading used in that work was 22 wt%. They demonstrated that the dispersed phase particle size could be controlled as a function of the TPS concentration.

In this work an improved and much more effective one-step approach for the preparation of LDPE/TPS blends is presented [30,31]. The purpose of this study was to analyze the effect of processing conditions, glycerol content and TPS composition on the morphology and properties of LDPE/TPS blends. An emphasis was placed on controlling highly continuous TPS phase morphologies.

2. Experimental

2.1. Materials

Two commercial LDPE resins, LDPE2040 (MFI = 12 g/10 min) and LDPE2049 (MFI = 20 g/10 min), were supplied by Rexene Chemical Co (now Huntsman). They are referred to as PE1 and PE2 respectively. Supergell 1203-C wheat starch obtained from ADM/Ogilvie was composed of 25% amylose and 75% amylopectin. TGA measurements showed that the water content in the starch granules was 7.1%. The water content of glycerol (SIMCO Chemical Products Inc.) was determined by its refractive index to be 5.9%.

2.2. Processing

Starch suspensions were prepared using the ratios of starch, glycerol and water listed in Table 1. Starch granules were gelatinized, plasticized and blended with LDPE in a one step process. The extrusion system (Fig. 1) was composed of a single-screw extruder (SSE) connected to a Leistritz AG 34 mm co-rotating twin-screw extruder (TSE) composed of eight zones. The starch suspension was fed in the first zone of the TSE. Three suspension compositions were used and are shown in Table 1. Native starch was gelatinized and plasticized in zones 2–4 of the TSE. Volatiles were extracted in the fourth zone at a temperature of 110 °C by venting under vacuum. Molten LDPE ($T = 150$ °C) was fed from the SSE to the fifth zone of the TSE using an adapter designed specially for that purpose. The mixing of TPS with LDPE ($T = 150$ °C) started in the same (fifth) zone and continued to the seventh zone of the TSE. The last (pumping) zone was used to increase the pressure of the extrudate ($T = 150$ °C). The TSE screw speed for all blends was 150 rpm. Blends were extruded through a 2.5 × 32 mm rectangular die. The extrudate was quenched in a calendar to form ribbons of about 2 mm thickness. A draw ratio [32] of approximately 2 was applied to these blends. LDPE/TPS blends were prepared containing 27–53% starch by weight. More details concerning the extrusion process are reported elsewhere [30].

Vapor extracted during extrusion was mainly composed of water, most of which was removed during the venting process. For that reason, the TPS can be considered as a binary blend of starch and glycerol. Under such conditions, the glycerol content of the TPS can be estimated directly from the glycerol content in the initial suspension. Hence the final glycerol content in the TPS after extrusion, prepared from suspensions containing 32, 27.5 and 20% glycerol, was 40, 36, and 29%, respectively. Thermoplastic starch materials prepared at these glycerol contents are referred to as TPS 40, TPS 36 and TPS 29 in this study.

2.3. On-line viscosity measurements

The extruder configuration was modified to evaluate the viscosity of pure components under the same conditions used for melt blending. Zones 5–7 were taken out of the TSE and the eighth zone was connected to the fourth one. This allowed the estimation of the viscosity of the PE and TPS at the same point at which mixing takes place. The rectangular die was replaced by a series of capillary dies (H1, H2, H3) that have an internal diameter of 0.328 cm. The L/D ratios of the capillary dies were 9.658, 15.491 and 23.183 for H3, H2, and H1, respectively. The flow rate of the starch suspension was fixed at 40 g min^{-1}, while the flow rate of TPS extrudate was varied using a valve placed on the extruder head. Pressure and temperature sensors (Dynisco, Franklin, MA) were placed far ahead of this valve to avoid flow disturbances. Pressure values were measured each 5 s while the TPS mass flow was determined at intervals of 30 s once the pressure was stable. Bagley's correction was performed using the data from the three capillary dies. Fig. 2 indicates the viscosity of PE1, PE2, TPS36 and TPS40. A more detailed study of the rheological properties of the thermoplastic starch is given elsewhere [33].

Table 1
Composition of starch suspensions

Code	Starch (%)	Glycerol (%)	Water (%)
TPS40	48	32	20
TPS36	48.5	27.5	24
TPS29	50	20	30

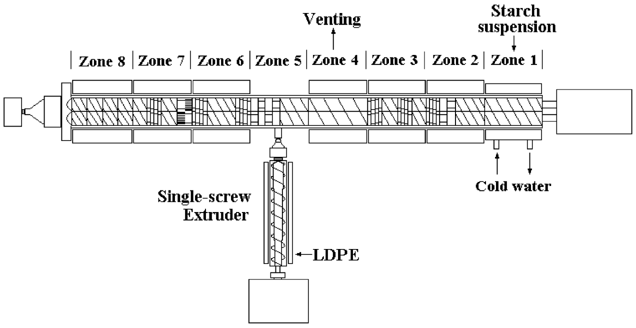

Fig. 1. Schematic representation of the one-step extrusion system used for the preparation of PE/TPS blends.

2.4. Scanning electron microscope

PE/TPS blend ribbons were cryogenically fractured to obtain surfaces both axial and transverse to the machine direction. Only axial views are shown in this paper since all transverse section demonstrated circular or quasi-circular forms [31]. Fractured samples were coated with a gold/palladium alloy and further observed in a JSM-820 SEM.

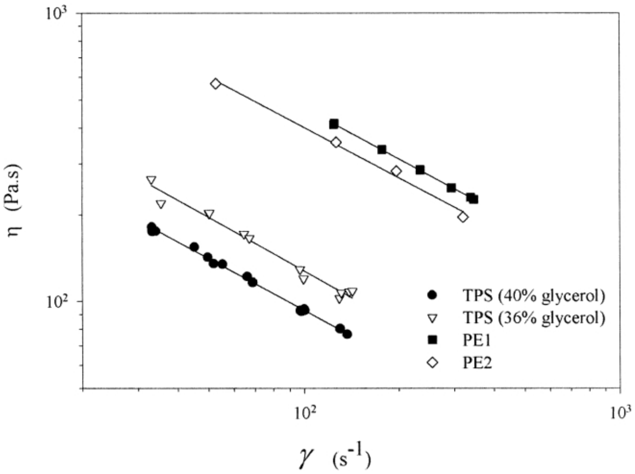

Fig. 2. Viscosity as a function of shear rate for PE1, PE2, TPS36 and TPS40 determined on-line from a five section TSE at 150 °C.

2.5. Thermogravimetry

The LDPE concentration was measured using a TGA 2950 (TA Instruments), equipped with a computer for data acquisition (Thermal Analysis 2000). The temperature was varied from 35 to 600 °C at a heating rate of 10 °C min^{-1}. Three well-defined shifts were observed in the TGA curves (Fig. 3). The first shift, at around 100 °C, was produced by water evaporation. The second shift started at ca. 180 °C and was due to the evaporation of glycerol. This continues gradually up to 300 °C where the thermal decomposition of starch occurs. Signal overlap precludes the direct calculation of the glycerol content by this technique. The last shift, at around 400 °C, is caused by the thermal decomposition of LDPE. TPS and PE/TPS blends produced a black residue after each measurement, which was related, but not directly proportional, to the thermal decomposition of starch. The LDPE concentration in the blend can be measured from the difference in weight at 400 and 575 °C.

2.6. Tensile testing

PE/TPS blends were tested according to the ASTM D-638 method. Tensile specimens of type IV were cut longitudinally from the recently prepared PE/TPS ribbons. In order to evaluate the effect of minor phase orientation, samples (type V) were cut parallel and perpendicular to the machine direction. Tests performed with those samples will be referred to as microtensile tests. Tensile samples were conditioned at ~50% relative humidity following the ASTM standard. Microtensile samples were conditioned at 0 and 50% relative humidity (RH) for 48 h. All samples were strained at 10 mm min^{-1} on a M30K machine (JJ Instruments) equipped with a 5 kN cell and a data acquisition system. The average values of the Young's modulus and elongation at break were calculated from at least 12 measurements.

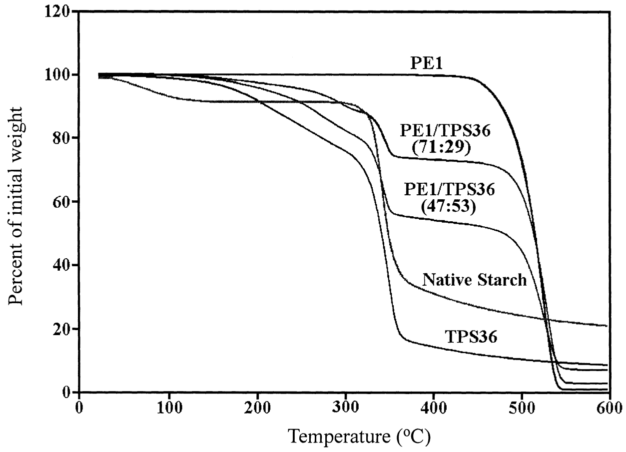

Fig. 3. Typical TGA curves of native starch, PE1, TPS36 and PE1/TPS36 blends measured from 35 to 600 °C at a heating rate of 10 °C min^{-1}.

2.7. Percent continuity

A sample of 1 mm length (machine direction) × 7.5 mm width × 2 mm thickness was cut from PE/TPS ribbons. Hydrolytic degradation of starch domains in those samples was carried out at 60 °C in a solution of HCl 6N for 96 h. Extracted samples were vigorously washed with distilled water and dried at 60 °C in a vacuum oven for 48 h. The extraction percentage was determined by the weight loss.

2.8. TPS refractive index

The average index of refraction (η) of TPS samples was measured at 23 °C according to ASTM Standard Test Method D524-90. Thin films of around 100 μm were prepared by compression molding at 70 °C using a dried TPS sample. Isopropylaniline ($\eta = 1.53$, at 25 °C) was used as the contacting liquid.

3. Results and discussion

3.1. Effect of glycerol content on morphology

PE/TPS blends display a discrete morphology where LDPE is the matrix, especially at low TPS content. The combined effect of glycerol content and the elongational flow exerted on PE/TPS blends (TPS concentration ≈ 30 wt%) during quenching can be observed in Fig. 4. PE1 blends prepared with TPS40 and TPS36 (Figs. 4(a) and (b)) show a high level of deformation in the machine direction. Conversely, blends compounded with TPS29 show very little deformation (Fig. 4(c)) and even less when prepared with PE2 (Fig. 4(d)). The singular morphologies displayed by PE/TPS blends are closely related to the differences in viscosity of both TPS and PE. The rheological properties of these TPS materials have been studied and it was found that 30% glycerol is required to effectively plasticize starch [33]. From Fig. 4, it can be seen that below that limit, the viscosity and elasticity of TPS are too high to allow the LDPE matrix to greatly deform the TPS dispersed phase. When the lower viscosity PE2 is used it can be seen in Fig. 4(d) that the dispersed particles of TPS are of a spherical nature and that the particle size has increased compared to those in Fig. 4(c). These results clearly demonstrate that a high degree of morphological control is possible for this system and that the full range from spherical dispersed phase to that of a highly deformed fibrillar phase can be obtained at a given TPS concentration level. In fact, it is apparent that the control of the glycerol concentration allows one to modify the state of the starch from that of a solid particle to that of a quasi crosslinked dispersed phase to that of a highly deformable material. It will be shown below that these different structures have an important influence on the mechanical properties.

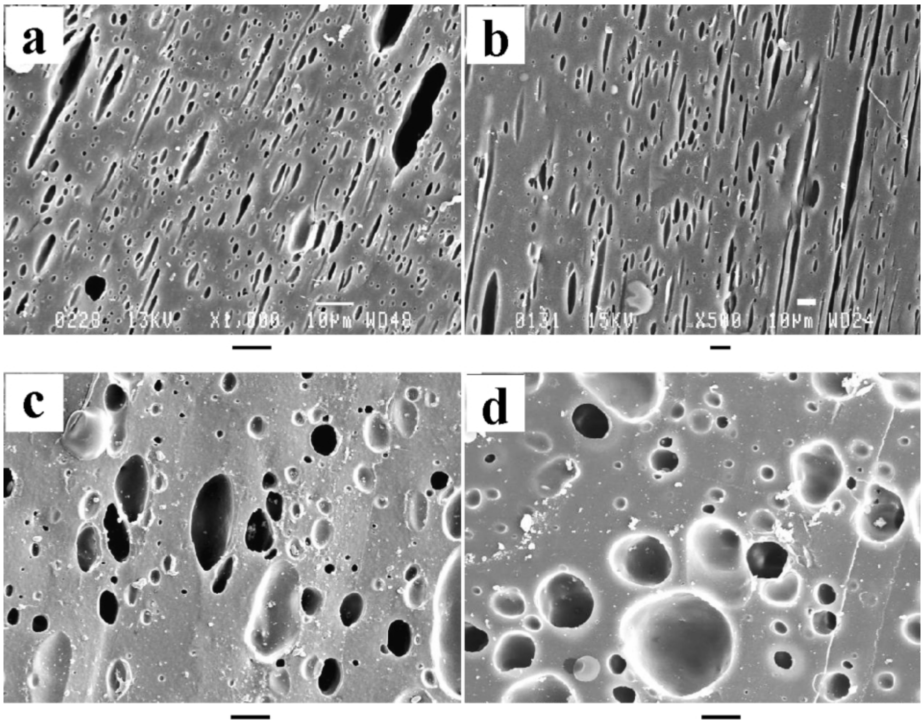

Fig. 4. Effect of glycerol content and LDPE viscosity on the morphology of microtomed PE/TPS (70/30) blends. PE1/TPS blends: (a) 40% glycerol, (b) 36% glycerol, and (c) 29% glycerol, (d) PE2/TPS at 29% glycerol content. The black bar below the micrographs represents 10 μm. Axial views.

3.2. *Effect of TPS concentration on morphology*

The axial direction morphology of PE1/TPS36 blends was a combination of large fiber-like structures with small spherical-like particles (Fig. 5). Increasing the TPS concentration reduces the number of small spherical particles due to particle-particle coalescence. The larger particle size of the TPS domains plus particle coalescence leads to the lengthening of TPS fibers in the machine direction. At high TPS loadings (above 45 wt%), it was

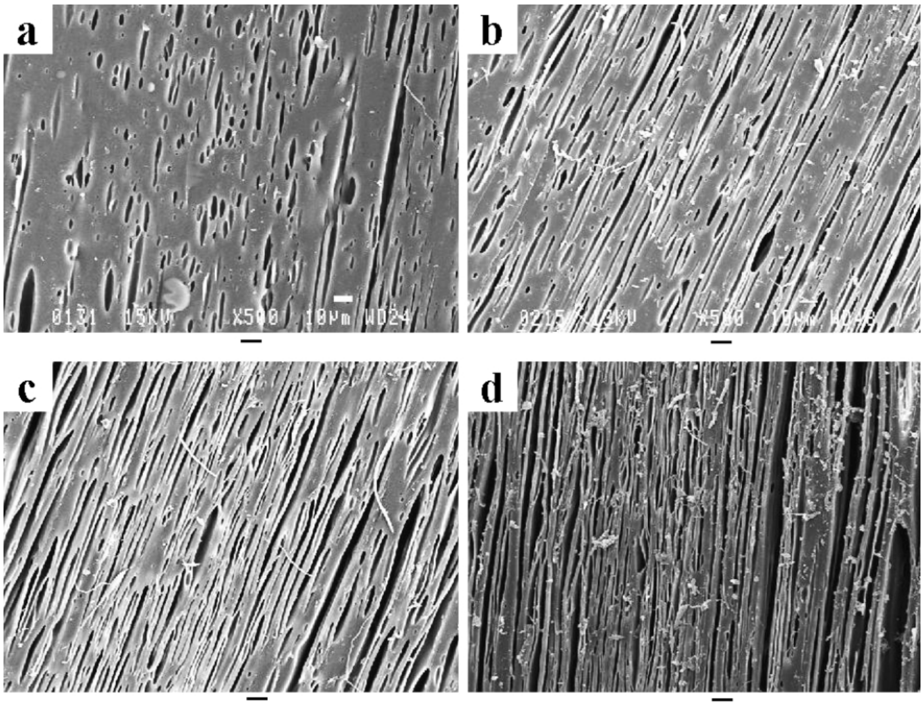

Fig. 5. Influence of TPS concentration on the morphology of PE1/TPS36 blends. (a) 29 wt% TPS, (b) 36 wt% TPS, (c) 45 wt% TPS, and (d) 53 wt% TPS. The black bar below the micrographs represents 10 μm. Axial views.

difficult to distinguish whether LDPE or TPS constituted the matrix. Both components appear to be fully continuous in the axial draw direction. The orientation imposed by the elongational flow field at the die exit plays an important role in the continuity development of starch in these PE/TPS blends.

The starch domain size increases in PE1/TPS29 as the TPS29 content increases (Fig. 6). However, in contrast to the high continuity observed for the low-viscosity low-elasticity TPS36, TPS29 particles remain dispersed in a PE1 matrix, even at high loadings (conc. of TPS ≈ 49 wt%). It can be observed from Fig. 6 that increasing the concentration of the TPS at low glycerol contents has little effect on the particle shape.

3.3. TPS continuity

Blends of PE/TPS having higher glycerol contents showed a fiber-like morphology in the machine direction. Consequently, a higher percent of continuity in the axial direction can be expected. In order to quantitatively determine the extent of this continuity, samples were exposed to hydrolytic extraction and the percent continuity was measured as a function of weight loss. The percent starch continuity as a function of TPS content for PE1/TPS36 and PE2/TPS29 blends is plotted in Fig. 7.

In all cases, the percent continuity of starch domains increases as TPS concentration increases and reaches 100% at the phase inversion region. In PE1/TPS36 blends, the starch phase could be completely extracted, an indication of very high continuity in the axial direction. It is interesting to note that the TPS continuity development for the PE2/TPS29 system is shifted to higher TPS concentrations. This is a result of the dominance of droplet morphologies discussed above. The TPS36 is highly elongated and percolates more readily while PE2/TPS29 develops continuity through essentially spherical particle–particle interactions and coalescence [34].

The high degree of TPS continuity demonstrated in this work indicates that these blend systems have the potential to render all starch domains in the blend accessible for biodegradation. Separate enzymatic biodegradation experiments will be required to verify this potential.

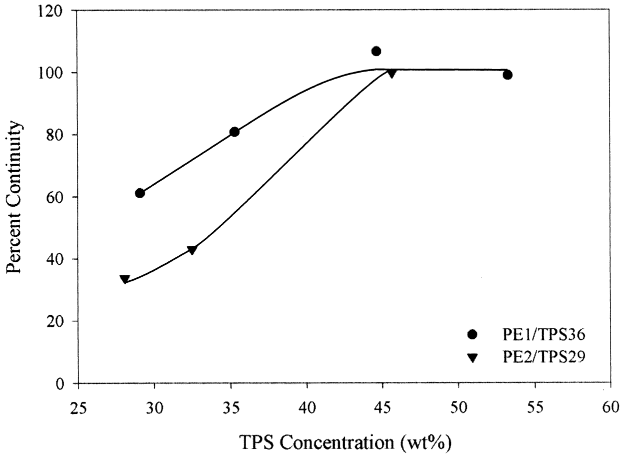

Fig. 7. Effect of glycerol content, PE type and TPS concentration on the percent continuity of PE1/TPS36 and PE2/TPS29 blends.

3.4. Mechanical properties

Elongation at break (ε_b). The relative elongation at break ($\varepsilon_b/\varepsilon_{b0}$) in the machine direction of PE1/TPS blends is shown in Fig. 8(a) and raw data are given in Table 2. The results are excellent and demonstrate that at high glycerol contents (36 and 40%), the blends have an ε_b comparable to the virgin polyethylene (ε_{b0}) even at 53 wt% TPS. The ε_b values of PE1 blends drop with the addition of TPS29. If these data are compared with the morphology results from the previous section, it is clear that the high ε_b for blends with TPS36 and TPS40 is closely related to the ability to deform the TPS phase.

In St-Pierre's work [18], PE/TPS blends presented a maximum in the ε_b at around 10 wt% TPS followed by a dramatic drop at 22 wt%. In this work, the improved extrusion process and the controlled deformation of the TPS phase yields an important improvement in the ε_b of PE/TPS blends as a function of composition, as observed in Fig. 8(a). Such an improvement in ε_b is also, in part, due to a highly effective removal of water by venting before blending with polyethylene. In St-Pierre's process, TPS was blended with LDPE and then passed through the venting section. At low concentration, TPS was probably encapsulated in a LDPE matrix, which impeded proper water removal. The presence of water at the blending

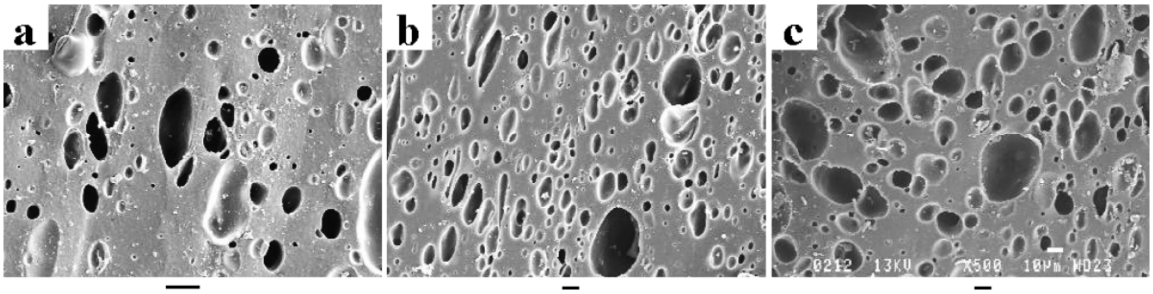

Fig. 6. Influence of TPS concentration on the morphology of PE1/TPS29 blends. (a) 30 wt% TPS, (b) 41 wt% TPS, and (c) 49 wt% TPS. The black bar below the micrographs represents 10 μm. Axial views.

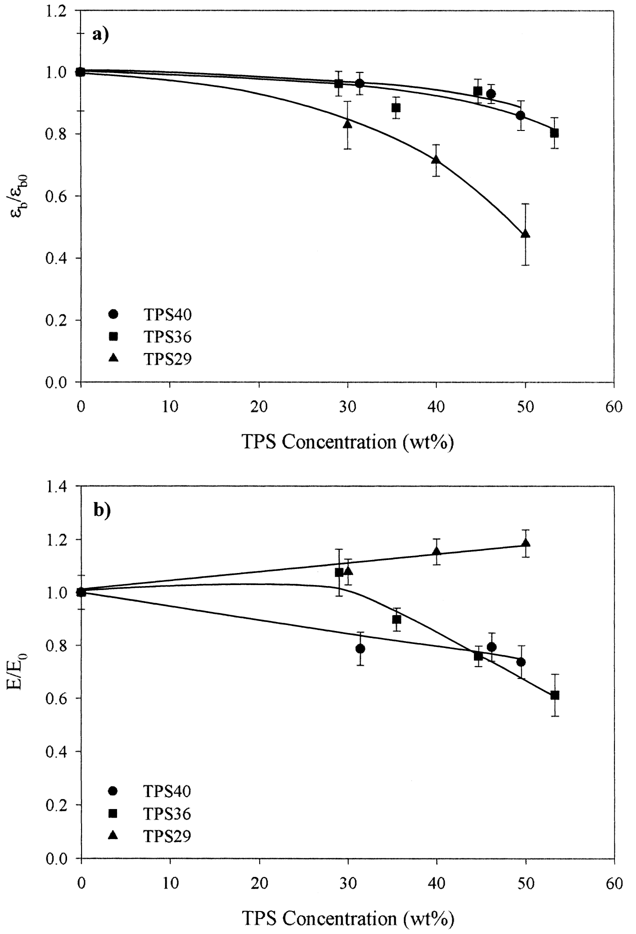

Fig. 8. (a) Relative elongation at break ($\varepsilon_b/\varepsilon_{b0}$) and (b) relative Young's modulus (E/E_0) of PE1/TPS blends as a function of TPS concentration (wt%). Terms with subscript 0 refer to the pure LDPE.

temperature (150 °C) can lead to the formation of bubbles in the extrudate, which weakens the final product [35]. In the present system, water was almost completely devolatilized from TPS before mixing with polyethylene [30]. Thermogravimetric analysis indicates the presence of only 1% of water in the final extruded product from the current work.

Table 2
Tensile properties of PE1/TPS blends in the machine direction

Material	TPS (wt%)	ε_b (%)	$\varepsilon_b/\varepsilon_{b0}$[a]	E (MPa)	E/E_0[a]	σ_{max} (MPa)	$\sigma_{max}/\sigma_{0max}$[a]
PE1	0	482	1.00	55.9	1.00	11.8	1.00
PE1/TPS40	31	465	0.97	44.0	0.79	9.7	0.83
	46	449	0.93	44.4	0.79	8.7	0.74
	50	415	0.86	41.2	0.74	8.7	0.74
PE1/TPS36	29	464	0.96	60.0	1.08	10.5	0.89
	36	427	0.89	50.1	0.90	9.8	0.83
	45	453	0.94	42.4	0.76	8.9	0.76
	53	388	0.80	34.2	0.61	8.2	0.69
PE1/TPS29	30	400	0.83	60.2	1.08	9.8	0.83
	41	345	0.72	64.4	1.15	9.6	0.82
	49	230	0.48	66.2	1.19	8.2	0.69

[a] Relative values were determined as a function of PE1.

Young's modulus. The relative Young's modulus (E/E_0) is demonstrated in Fig. 8(b) and the raw data are given in Table 2. Once again the results are excellent. E can be maintained at high levels even at high loadings of TPS36 and TPS40. At lower levels of glycerol (TPS29) the E of the blend can be seen to even exceed that of the neat polyethylene. These are unusual results considering the high levels of immiscibility between PE and TPS. The results also indicate the potential of tailoring the mechanical properties of the blend through an appropriate glycerol content. This unexpected result can be explained by good interfacial contact. Leclair and Favis found that the compression exerted by a crystalline matrix (HDPE), during crystallization, on an amorphous dispersed phase (PC) can result in good interfacial contact and a higher elastic modulus [36]. They also observed that this effect had a positive influence on the modulus only when the contraction took place on a smooth, non-deformable surface. The mirror-like quality of the TPS surface is demonstrated in Fig. 9.

Ultimate tensile strength (σ_{max}). As in the cases of the modulus and the elongation at break, PE/TPS blends maintained a high percentage of the ultimate tensile strength of pure PE (σ_{0max}) even at high TPS loadings (Table 2). The 50:50 PE/TPS blend prepared with TPS 40 maintains 74% of the ultimate tensile strength of pure PE.

Effect of humidity on axial and cross properties. Microtensile samples cut in the machine direction (Fig. 10) showed a similar trend as that observed for the standard tensile test (Fig. 8). The humidity conditioning of blends compounded with high glycerol contents (36 and 40%) at 0 and 50% of relative humidity (RH) has little effect on the tensile properties. This is an important finding since it indicates that a control of glycerol levels in the TPS can dramatically reduce the sensitivity of these types of materials to humidity in the environment and opens up a

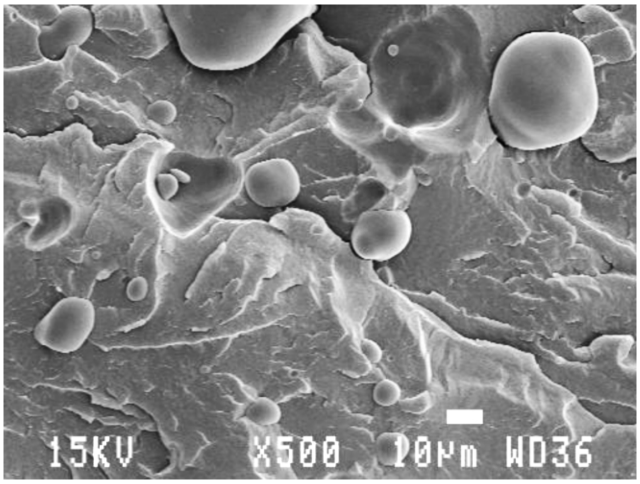

Fig. 9. SEM cryofracture surface of PE1/TPS demonstrating excellent interfacial contact and mirror-like surface of the TPS phase. Axial view.

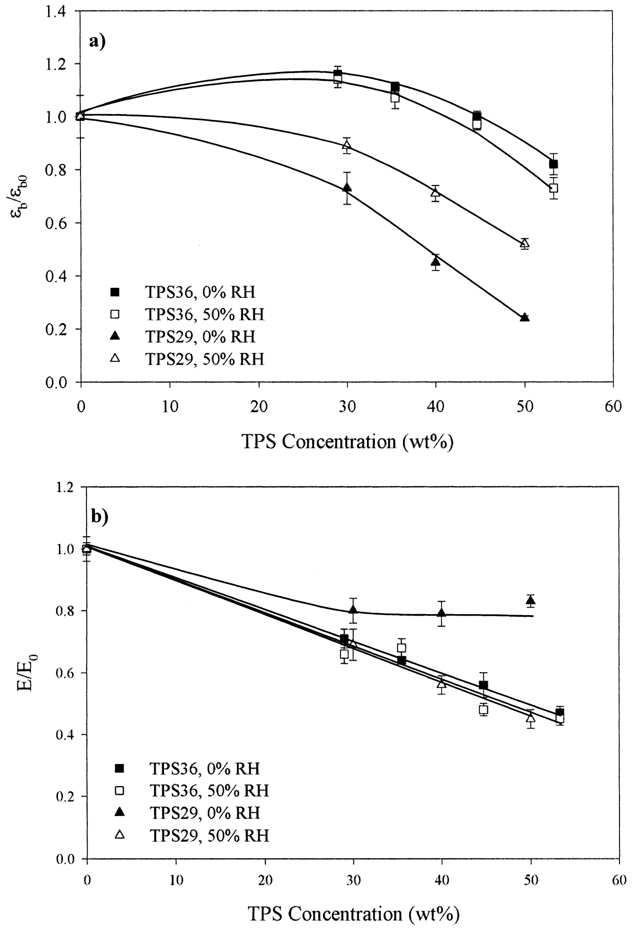

Fig. 10. Effect of humidity on (a) the relative elongation at break ($\varepsilon_b/\varepsilon_{b0}$) and (b) the relative Young's modulus (E/E_0) of PE1/TPS36 and PE1/TPS29 microtensile samples (machine direction). Filled symbols: conditioned at 0% RH; open symbols: conditioned at 50% RH.

wide range of application areas. It should be noted that in a separate study [30] we have examined the properties of this same blend after one year of ageing and conditioned at ~50% RH and found only a very small decrease in the elongation at break and modulus. On the other hand, blends containing 29% of glycerol are more sensitive to humidity. When the relative humidity increased from 0 to 50%, the ε_b increased (Fig. 10(a)) and the E decreased (Fig. 10(b)) because of the softening effect of water on the TPS dispersed phase.

The mechanical properties of microtensile samples cut in the cross direction are listed in Table 3. Due to the axial orientation imposed during calendaring, the cross properties of PE1 and PE1/TPS microtensile samples display a reduction with respect to those in the axial direction (Table 3). For instance, values of ε_b and E for the pure PE1 conditioned at 0% RH drop from 625 to 222 and from 54.1 to 43.3, respectively. In the case of the PE1/TPS36 blends, the elongation at break values are significantly less than that observed in the longitudinal direction. Nevertheless, under all conditions studied, and despite the applied longitudinal draw ratio, the PE1/TPS36 blends demonstrate ductile behavior in the cross direction. These are excellent results considering that no interfacial modifier was used in these blends. Under all conditions, PE1/TPS29 blends demonstrate higher elongations at break in the cross direction. Because of its isotropic structure composed of spherical dispersed TPS particles, the cross direction properties of PE1/TPS29 blends are less affected than the blends exhibiting a fiber-like structure. As mentioned above, the spherical dispersed phase morphology in PE1/TPS29 blends results from its less deformable TPS phase. These results clearly demonstrate that the morphology of the TPS dispersed phase plays a very important role on the cross microtensile properties of PE1/TPS blends. The reduction in the section area, transverse to the machine direction, presented by fiber-like domains leads to the drop in the ε_b of PE1/TPS36 blends. Conversely, spherical particles have the same surface area in both axial and cross direction, which permitted a good balance of tensile properties in both testing directions. These results indicate that a significant degree of property manipulation can be achieved through morphology control via the melt drawing and the glycerol content in the TPS.

Table 3
Tensile properties of PE1/TPS microtensile specimens in the cross direction conditioned at 0 and 50% RH

Material	TPS (wt%)	ε_b (%)	$\varepsilon_b/\varepsilon_{b0}$[a]	E (MPa)	E/E_0[a]
Axial/0% RH					
PE1	0	625	–	54.1	–
Cross/0% RH					
PE1	0	222	1.00	43.3	1.00
Cross/0% RH					
PE1/TPS36	29	85	0.38	36.0	0.83
	36	62	0.28	35.0	0.81
	45	43	0.19	25.3	0.58
	53	33	0.15	24.5	0.57
PE1/TPS29	30	163	0.73	42.7	0.99
	41	84	0.38	40.7	0.94
	49	41	0.19	43.8	1.01
Cross/50% RH					
PE1/TPS36	29	90	0.40	31.3	0.72
	36	71	0.32	27.0	0.62
	45	49	0.22	18.1	0.42
	53	39	0.18	14.0	0.32
PE1/TPS29	30	454	2.05	33.8	0.78
	41	256	1.16	30.8	0.71
	49	205	0.92	24.5	0.57

[a] Relative values were determined as a function of PE1 (cross) conditioned at 0% RH.

3.5. Interfacial structure

In addition to the high ductility shown by the one-step processed LDPE/TPS blends in this work, these blends also demonstrated high levels of transparency even at high loadings of TPS. Opacity in immiscible polymer blends originates from two possible sources: different refractive indexes (η) between the two domains or scattering of light due to interfacial voids. This is depicted in Fig. 11. The η has been related to the molecular arrangement and orientation of polymer chains [37]. As the molecular packing increases, such as is found in crystalline structures, the η increases. In the case of semi-crystalline polymers, such as PE, the η is reported as the average between the crystalline (1.560) and amorphous (1.476) regions. The average η of PE1, considering its density ($\rho = 0.920$ g cm^{-3}) should be around 1.514 [38]. Comparing that value with those determined for TPS40 and TPS36 (1.489 ± 0.001 and 1.491 ± 0.001, respectively), a difference of ca. 0.024 was obtained. This difference would be even smaller if amorphous LDPE was preferentially located at the interface with TPS. This difference in refractive index is similar in magnitude to the refractive index difference between water ($\eta = 1.333$) [39] and glass ($\eta = 1.356$, glass standard #1, ASTM D542-90) and represents too small a value to result in opacity.

The other potential cause of opacity in immiscible polymer blends is the formation of microvoids at the interface resulting from poor surface adhesion and the different thermal expansion coefficients of matrix and dispersed phase. As previously discussed, PE/TPS blends display an excellent interfacial contact. This is likely due to the contraction of the semi-crystalline polyethylene about the amorphous TPS during cooling. Previous work has shown that such a contraction can significantly reduce interfacial voiding [36]. The micrograph in Fig. 9 demonstrates the excellent interfacial contact.

An argument could be raised that very small microvoids might be still present beyond the range of typical microscopic techniques. Even if very small microvoids existed at the interface it is highly probable that a very thin glycerol layer coats the surface of TPS in these materials. Since TPS is a miscible starch/glycerol mixture and since the glycerol/PE and starch/PE interfacial tensions are quite similar (23.17 and 23.95 mN m^{-1}, respectively, as estimated using the harmonic mean approach) it is very likely that some low molecular weight glycerol migrates to the TPS/PE interface in order to reduce the overall surface free energy of the blend system as predicted by Harkin's equation rewritten by Hobbs and coworkers [40]. This phenomenon would have the effect of even further reducing the optical effects due to interfacial voiding.

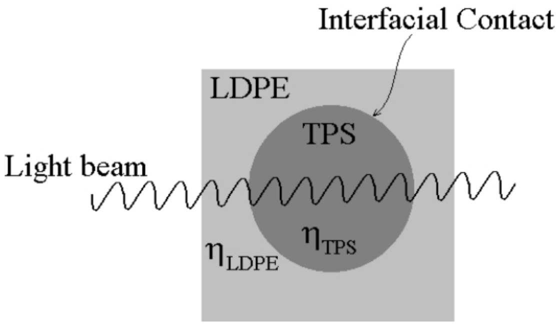

Fig. 11. Schematic representation of the PE/TPS interface. These blends demonstrate high levels of transparency at high TPS loadings due to similar refractive index values for the PE and the TPS as well as due to the high level of interfacial contact (very little interfacial microvoiding).

It is apparent from this work that a combination of excellent interfacial contact and very similar refractive index values are responsible for the high levels of transparency demonstrated by this immiscible polymer blend (Fig. 11).

4. Conclusions

This study reports on a polymer blend material comprised of polyethylene and thermoplastic starch possessing unique properties prepared using a novel one-step process. The PE/TPS blends demonstrate levels of ductility and modulus similar to the virgin polyethylene even at very high loadings of TPS without the addition of any interfacial modifier. The excellent properties are a combination of both the melt blending process and a sophisticated morphology control. Furthermore, the material demonstrates very high levels of transparency even at 50:50 concentrations of PE/TPS.

The melt blending is carried out in the TSE to produce ribbon extrudates and the first part of the process converts a starch–water–glycerol slurry into a virtually water-free thermoplastic starch. Polyethylene is added to the thermoplastic starch as a melt using a SSE connected midway on the twin-screw. The latter part of the twin-screw blends the two melts through intensive mixing zones. Using this approach it is possible to achieve blends where the thermoplastic starch morphology can be effectively controlled yielding a wide range of sophisticated morphological states.

Through a control of the glycerol content and thermoplastic starch volume fraction, the above process can result in morphological structures which run the full range of those observed in classical blends of synthetic thermoplastics. Spherical, fiber-like and co-continuous morphologies are observed. Control of the glycerol content of the starch allows one to control the properties of starch from that of a solid filler through to that of a highly deformable thermoplastic material. A wide range of potential properties can be exploited for this type of material.

At 55:45 PE/TPS, and when the thermoplastic starch in the blend is highly continuous, the blend material at 36% glycerol in TPS content maintains 94% of the elongation at break and 76% of the modulus of polyethylene without the addition of any interfacial modifier. At a composition level of 71:29 PE/TPS for the same glycerol content, the blend retains 96% of the elongation at break and 100% of the modulus of polyethylene. These properties surpass any results ever obtained through the addition of dry granular starch and are achieved despite the high levels of immiscibility in the polar-nonpolar TPS–PE system. Even the properties in the cross-direction demonstrate ductility at these high concentrations. At 36% glycerol contents in the TPS, the blend system demonstrates only very low levels of sensitivity to moisture. A high degree of transparency is maintained over the entire concentration range due to the similar refractive indices of PE and TPS and the virtual absence of interfacial voiding.

This material has the added benefit of containing large quantities of a renewable resource and hence represents a more sustainable alternative to pure synthetic polymers. Since the starch can be fully interconnected through morphology control, it is also completely accessible for biodegradation as opposed to the case of starch particles dispersed in a synthetic polymer matrix. Separate enzymatic biodegradation experiments are underway to verify this potential.

This approach to blending with TPS is currently being adapted to other polymers such as polypropylene and biodegradable polyester materials and will be discussed in future papers.

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada. Mr Rodriguez Gonzalez thanks the Mexican Council of Science and Technology (CONACyT) for financial support during his PhD studies. The authors would also like to thank Professor Suzanne Lacroix of the Engineering Physics Department and Pei Lian Ma of the Chemical Engineering Deparment of the École Polytechnique de Montréal for helpful discussions.

References

[1] Evangelista RL, et al. Ind Engng Chem Res 1991;30:1841.

[2] Willett JL. J Appl Polym Sci 1994;54:1685–95.

[3] Griffith GJL. US Patent 4 021 388; 1977.

[4] Kim YJ, Lee HM, Park OO. Polym Engng Sci 1995;35:1652.

[5] Chandra R, Rustgi R. Polym Degrad Stabil 1997;56:185.

[6] French D. Starch chemistry and technology. New York: Academic Science; 1984.

[7] Otey FH, Westhoff RP, Doane WM. Ind Engng Chem Prod Res Dev 1980;19:592–5.

[8] Otey FH, Westhoff RP. US Patent 4,337,181; 1982.

[9] Otey FH, Westhoff RP, Doane WM. Ind Engng Chem Res 1987;26: 1659–63.

[10] Wool RP, Oelschlaeger P, Willett J. PCT Patent WO 90/14388; 1990.

[11] Shi B, Seib PA. Proc. ACS Div Polym Mater Sci Engng, Proceeding of the 1995 Spring ACS meeting; v 72, p. 188.

[12] Fanta GF, Swanson CL, Shogren RL. J Appl Polym Sci 1992;44: 2037–42.

[13] Shogren RL, Thompson AR, Greene RV, Gordon SH, Cote G. J Appl Polym Sci 1991;42:2279–86.

[14] Shogren RL, Greene RV, Wu YV. J Appl Polym Sci 1991;42:1701–9.

[15] Shogren RL, Thompson AR, Felker FC, Harry-O'Kuru RE, Gordon SH, Greene RV, Gould JM. J Appl Polym Sci 1992;44:1971–8.

[16] Dehennau C, Depireux T. European Patent EP 0 554 939 A2; 1993.

[17] Aburto J, Thiebaud S, Alric I, Borredon E, Bikiaris D, Prinos J, Panayiotou C. Carbohydr Polym 1997;34:101–12.

[18] St-Pierre N, Favis BD, Ramsay BA, Ramsay JA, Verhoogt H. Polymer 1997;38:647–55.

[19] Bikiaris D, Prinos J, Panayiotou C. Polym Degrad Stab 1997;56:1–9.

[20] Bikiaris D, Prinos J, Panayiotou C. Polym Degrad Stab 1997;58: 215–28.

[21] Bikiaris D, Prinos J, Koutsopoulos K, Vouroutzis N, Pavlidou E, Frangis N, Panayiotou C. Polym Degrad Stab 1998;59:287–91.

[22] Prinos J, Bikiaris D, Theologidis S, Panayiotou C. Polym Engng Sci 1998;38(6):954–64.

[23] Averous L, Moro L, Dole P, Fringant C. Polymer 2000;41:4157–67.

[24] Averous L, Fringant C. Polym Engng Sci 2001;45(5):727–34.

[25] Averous L, Dole P, Martin O, Schwach E, Couturier Y. Symposium de la société Polymérique du Québec, Nancy (France); 2001.

[26] Averous L, Fauconnier N, Moro L, Fringant C. J Appl Polym Sci 2000;76:1117–28.

[27] Martin O, Averous L. Polymer 2001;42:6209–19.

[28] Walia PS, Lawton JW, Shogren RL, Felker FC. Polymer 2000;41: 8083–93.

[29] Walia PS, Lawton JW, Shogren RL. J Appl Polym Sci 2002;84: 121–31.

[30] Favis BD, Rodriguez F, Ramsay BA. US Patent Appl. No. 09/472, 242; 1999 (accepted).

[31] Rodriguez-Gonzalez FJ, Ramsay BA, Favis BD. Proc Annu Tech Conf ANTEC'99 New York (USA) 1999;57(2):2770–4.

[32] Gonzalez-Nunez R, De Kee D, Favis BD. Polymer 1996;37(21): 4689–93.

[33] Rodriguez-Gonzalez FJ, Ramsay BA, Favis BD. Proceedings of 17th Annual Meeting of Polymer Processing Society, Montreal (Canada); 2001. p. 312–9, submitted for publication.

[34] Li J, Ma PL, Favis BD. Macromolecules 2002;35(6):2005–16.

[35] Verhoogt H, Truchon FS, Favis BD, St-Pierre N, Ramsay BA. Proceedings of the Annual Technical Conference ANTEC'95. ; 1995. p. 2028–32.

[36] Leclair A, Favis BD. Polymer 1996;37(21):4723.

[37] Seferis JC, Samuels RJ. Polym Engng Sci 1979;19(14):975–94.

[38] Brandrup J, Immergut EH. Polymer handbook, 3rd ed. New York: Wiley; 1989.

[39] Budavari S. The Merck index, Eleventh ed. New Jersey: Merck and Co., Inc; 1989.

[40] Hobbs SY, Dekkers MEJ, Watkins WH. J Mater Sci 1988;23:1219.