Chapter from the book *Thermoplastic Elastomers*
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1. Introduction

Starch is a natural polymer synthesized by green plants as energy source. In comparison with low-cost synthetic polymers, starch is inexpensive, abundant and renewable raw material for the development of polymeric sustainable materials. It has been used in its native granular form as rigid filler or transformed in a thermoplastic material for melt blending with synthetic or natural polymers. Polymers filled with dry starch granules behave as typical composite materials where modulus increases and ductility decreases due to the stiffening effect of the starch granules (Willett, 1994, Kim et al, 1995, Chandra & Rustgi, 1997). An important disadvantage showed by polymeric composites filled with granular starch is the low starch content that can be added, especially for application where high ductility is required (Griffith, 1977). In contrast to the ordered structure of starch molecules in granular starch, thermoplastic starch (TPS) is an amorphous material that can flow and be deformed as any synthetic polymer (St.-Pierre et al., 1997). Crystallinity of starch granules is destroyed by the application of heat and shear in the presence of moisture during the gelatinization process. The addition of a good plasticizer, such as glycerol, allows TPS to be extruded at the processing temperatures of most commodity polymers (St.-Pierre et al., 1997). Mechanical performance of TPS material blended with synthetic polymers depends on a series of parameters including blend morphology (particle size and shape, and particle dispersion and distribution), interfacial adhesion and the intrinsic characteristics of TPS (Rodriguez-Gonzalez et al., 2003b). It has been reported that melt blending of TPS with synthetic polymer is an excellent alternative for the development of sustainable and more environmentally friendly product (Rodriguez-Gonzalez et al., 2003b).

2. Thermoplastic starch preparation

The gelatinization of starch is a process that permits the release of starch macromolecules from granules. It can be carried out by exposing starch granules to heat and shear in the presence of moisture. In the gelatinization of starch during extrusion, it is important to have strict control of the energy applied and the moisture content. The gelatinization process is depicted in Figure 1. The application of excessive heat and shear, such as that observed during extrusion processing of starch at low moisture content, leads to its thermo-mechanical degradation (Gomez & Aguilera, 1983, 1984, Lai & Kokini, 1991). Products of starch degradation are mainly dextrin, and in more extreme cases oligomer and sugar (Gomez & Aguilera, 1983, 1984). Once starch granules are disrupted, the resulting gelatinized starch (GS) can be mixed with a
suitable plasticizer to reduce its melting temperature and improve its processability. This material is known as thermoplastic starch (TPS).

![Thermoplastic Elastomers Diagram](https://www.intechopen.com)

Fig. 1. Schematic representation of starch gelatinization and plasticization processes during extrusion.

Water is a good plasticizer for TPS but its use leads to a high dependence of final properties to environmental conditions of humidity. Utilization of plasticizers other than water helps to stabilize the properties of TPS. The main plasticizer used in TPS composition is glycerol (Forssell et al. 1997; Mathew & Dufresne, 2002; Souza & Andrade, 2002; Ma & Yu, 2004a; Ma & Yu, 2004b; Parra et al., 2004; Rodriguez-Gonzalez et al., 2003a; Rodriguez-Gonzalez et al., 2003b; Rodriguez-Gonzalez et al., 2004; Mali et al., 2005; Chand et al., 2006; Ma et al, 2006; Teixeira et al., 2007; Talja et al., 2007; Talja et al., 2008; Tena-Salcido et al., 2008; Chaudhary, 2010; Mendez-Hernandez et al., 2011) but other alcohols (Da Roz et al., 2006), polyols (Mathew & Dufresne, 2002; Parra et al., 2004; Mali et al., 2005; Da Roz et al., 2006; Talja et al., 2007; Chaudhary, 2010), sugars (Da Roz et al., 2006; Teixeira et al., 2007; Talja, 2008) or nitrogen compounds such as ethanolamine (Ma et al, 2006), formamide (Ma & Yu, 2004a; Ma & Yu, 2004b), acetamide (Ma & Yu, 2004a) or urea (You et al., 2003; Ma et al, 2006) have also been successfully employed. TPS materials have been prepared using casting process (Mathew & Dufresne, 2002; Parra, et al., 2004; Mali et al., 2005; Chand et al., 2006; Talja et al., 2007; Talja, 2008) or by melt mixing in batch, internal mixer (Forssell et al. 1997; Da Roz et al., 2006; Teixeira et al., 2007), or continuous equipment such as single (Souza & Andrade, 2002; Ma & Yu, 2004a; Ma & Yu, 2004b; Ma et al, 2006) or twin-screw extruders (Rodriguez-Gonzalez et al., 2003a; Rodriguez-Gonzalez et al., 2003b; You et al., 2003; Rodriguez-Gonzalez et al., 2004; Tena-Salcido et al., 2008; Chaudhary, 2010; Mendez-Hernandez et al., 2011). In the case of melt mixing processes, starch, plasticizer and water have been fed as dry blends (Ma & Yu, 2004a; Ma & Yu, 2004b; Da Roz et al., 2006; Ma et al, 2006; Chaudhary, 2010) or slurries (Rodriguez-Gonzalez et al., 2003a; Rodriguez-Gonzalez et al., 2003b; Rodriguez-Gonzalez et al., 2004; Tena-Salcido et al., 2008; Mendez-Hernandez et al., 2011). In some cases, TPS materials prepared by melt mixing have a significant water content which limits the
processing temperature far below the processing conditions of most synthetic polymers, i.e. >150°C, in order to avoid water vapor bubbles into TPS extrudates (Souza & Andrade, 2002; Farhat et al., 2003; Ma et al, 2006; Chaudhary, 2010). The development of an extruder configuration having a venting zone after both starch gelatinization and plasticization processes were accomplished and before exiting from the die allowed the preparation of water-free TPS (Favis et al., 2001; Favis et al., 2003, Favis et al., 2005).

3. Rheological and thermal properties of water-free TPS

The rheological and thermal properties of water-free TPS materials having high glycerol contents (29, 36 and 40%) were evaluated by DSC analysis and rheological measurements in shear and oscillatory modes (Rodriguez-Gonzalez et al., 2004). TPS materials were labeled according to their glycerol content. Hence, TPS29,33, TPS36 and TPS40 have 29, 33, 36 and 40% of glycerol.

Fig. 2. DSC thermograms of TPS samples conditioned for 24h at 0% R.H. The glycerol content in TPS is 40, 36 and 29% from the top to the bottom.

As previously mentioned, TPS materials prepared in this work are almost water-free starch-glycerol systems. Compared with previous work, TPS materials prepared in this work are binary systems which allow a more straightforward evaluation of the effect of glycerol on the thermal transitions of starch. DSC analysis of TPS shows a thermal transition below ambient temperature that decreases as glycerol content increases (Figure 2). On the other hand, no thermal transitions are observed between 25 and 200°C (not shown). The Tg of TPS decreases from −45 to −56°C as glycerol content increases from 29% to 40%. Van Soest et al. have reported the Tg of extruded TPS materials containing a starch/water/glycerol ratio of 100:27:5 of ±59°C (Van Soest et al., 1996). Forssell et al. (1997) studied the thermal transition of TPS materials prepared in a melt mixer as a function of glycerol and water content. Depending upon the composition, TPS materials presented one or two thermal transitions. In that work, at the lowest water content (ca. 1%) the upper transition of TPS decreases from
145 to 70°C as the glycerol content is increased from 14 to 29% while only TPS compounded with 29 and 39% glycerol showed lower transitions both at \( \approx -50^\circ\text{C} \). The upper transition was attributed to starch-rich phase while the lower transition was related to a starch-poor phase. Lourdin and coworkers prepared TPS cast films by mixing starch with different amounts of water and glycerol (Lourdin et al., 1997a; Lourdin et al., 1997b). Films having around 13% water content showed a reduction of Tg from 90 to 0°C when glycerol content increased from 0 to 24% (Lourdin et al., 1997a). In that case they observed a glassy to rubbery transition of TPS at around 15% glycerol. In a further paper, they compared the Tg of TPS films having around 11% water with respect to glycerol content and they found that Tg decreased from 126 to 28°C when glycerol content was increased from 0 to 40% (Lourdin et al., 1997b). Discrepancies in Tg values as a function of glycerol content can be related, as mentioned by Kalichevsky to the mixing history during TPS preparation (Kalichevsky et al., 1993).

During on-line measurements, TPS extrudates did not present bubbles due to the almost absence of water. The pressure readings of TPS36 and TPS40 at 150°C were quite regular while those of TPS29 were mostly irregular. For this reason only TPS36 and TPS40 were evaluated. As observed by other authors (Aichholzer and Fritz, 1998; Della Valle et al., 1992; Lai and Kokini, 1990; Senouci and Smith, 1988; Willett et al., 1995; Willett et al., 1998), the viscosity (\( \eta \)) of both TPS and PE1 melts display a power-law (shear thinning) behavior at the shear rate (\( \dot{\gamma} \)) interval developed over die extrusion conditions (Figure 3). The \( \eta \) of TPS materials depends on the plasticizer content. An increment of glycerol content from 36% to 40% results in a reduction of 20% of \( \eta \) of TPS36 (at \( \dot{\gamma} \sim 130 \text{ s}^{-1} \)).

![Graph](Fig. 3. Comparison of the viscosity of TPS40, TPS36 and PE1 measured on-line in the TSE at 150°C.)
Fig. 4. Effect of glycerol content on (a) elastic modulus ($G'$) and (b) loss modulus ($G''$) of TPS materials evaluated at 150ºC.
TPS exhibits the rheological behavior of a typical gel as characterized by a storage modulus ($G'$, Figure 4a) larger than the loss modulus ($G''$, Figure 4b) and with both moduli largely independent of frequency over the amplitude of the experimental window (Ross-Murphy, 1995). This behavior is produced by the presence of an elastic network embedded in a softer matrix. The rigidity in those regions can be produced by chemical or physical crosslinking. The structure of the elastic network has been related to the crystallinity derived from the complexation reaction between amylose and lipids (Conde-Petit & Escher, 1995; Della Valle et al., 1998) and the physical entanglement of the high molecular weight polysaccharides (Della Valle et al., 1998; Ruch and Fritz, 2000).

As expected, the augmentation of the glycerol content in TPS results in a reduction of both $G'$ and $G''$. However, the trend in the modulus curves was nearly the same, regardless of the glycerol content. From the study of low-concentration starch dispersions, Conde-Petit and Escher (1995) showed that the formation of amylose-emulsifier complexes modifies the viscoelastic response of potato starch dispersions. Crystalline regions produced during the amylose-emulsifier complexation form an elastic network, which is responsible for the liquid-like to solid-like viscoelastic modification. From the similarity of the trend of the $G'$ curves shown in Figure 4a, it can be inferred in this work that glycerol variation does not affect the nature of the hypothetical crystalline elastic network, it just plasticizes the amorphous fraction of starch.

The study of the viscoelasticity of starch-based materials has mainly focused on concentrated gels and dispersions ($\leq 5\%$ starch). In this work, the viscoelastic behavior of water-free TPS at high glycerol contents has been evaluated at 150°C. $G'$ decreases as glycerol content increases and the changes are similar at both low and high frequencies. Della Valle and co-workers also studied the behavior of a water-free TPS at 150°C and found that the decrease of $G'$ with glycerol content was dependent on frequency (Della Valle et al., 1998). However, that material was obtained by subjecting the TPS to a separate drying step, a process which can induce structural changes in the starch. The proportional reduction of $G'$ as a function of glycerol content observed in this work is similar to that observed in starch gel systems (Kulicke et al., 1996). Figure 6a shows that the reduction of the glycerol content from 40% to 33% results in a quasi-linear increment of $G'$, while the reduction from 33% to 29% glycerol produces a larger variation in $G'$. In the case of the elastic modulus of polymer composites, percolation theory explains the non-linearity produced by the phase inversion effect at high filler content (Willett, 1994). The limit of glycerol plasticization that produces the non-linearity observed in the $G'$ of TPS at a concentration around 30% glycerol can be explained in a similar way. TPS can be considered as a homogeneous system composed of a hard elastic network and soft amorphous regions. Amylose complex crystallites, highly entangled starch molecules, poorly plasticized starch-rich sites, or a combination of them could compose the hard elastic network. Soft amorphous regions could be composed of well-plasticized glycerol-rich starch. Even though the elastic network is present at 33% glycerol, the soft amorphous regions dominate the viscoelastic response. Increasing glycerol content, beyond this concentration, produces a relatively small reduction in the rheological parameters. On the other hand, below 30% glycerol the phase inversion of a soft to a hard matrix occurs resulting in the domination of the viscoelastic response by the hard elastic network, which is in good agreement with percolation theory. That suggests a glycerol plasticization threshold at a concentration around 30%.
4. Blending with polyethylene

Blending TPS with synthetic polymers have shown the typical characteristics of immiscible polymer blends (St-Pierre et al., 1997). The melt blending of TPS with synthetic polymers has given place to a series of scientific and technologic developments. Such works differed in the mixing protocol and the type of additives used. Some authors proposed the use of two steps for the preparation of TPS-based blends (Aburto et al., 1997, Bikiaris et al., 1997a, 1997b, 1998, Prinos et al., 1998, Averous et al., 2000a, 2000b, 2001a, 2001b, Martin & Averous, 2001) while other preferred just one-step processes (Dehennau & Depireux, 1993, St-Pierre et al., 1997). Starch-based blends prepared in two steps are generally characterized for the preparation of TPS in a separated extrusion step. St-Pierre and coworkers presented a one-step blending process for TPS-based polymer blends (St-Pierre et al., 1997). They developed an extrusion system combining a TSE with a single-screw extruder (SSE). TPS was prepared in the SSE, and then it was blended with LDPE in the last sections of the TSE. Using such an extrusion system, they demonstrated experimentally that a certain morphological control of PE/TPS blends could be achieved by varying the TPS concentration from 0 to 22 wt%. Those blends showed an unusual high level of ductility.

Fig. 5. Schematic representation of the one-step extrusion system designed for the melt blending of LDPE with water-free TPS.

An improved approach for LDPE/TPS blends in a one-step process was developed by Rodriguez-Gonzalez and coworkers (Rodriguez-Gonzalez et al., 2003b). It consisted of an extrusion system equipped with a single-screw extruder, from which molten LDPE is fed to the middle section of a twin-screw extruder. Suspensions of starch, glycerol and water were
fed to the hopper of the twin-screw extruder and, as described in section 3, water-free TPS having 29, 36 and 40% glycerol (TPS29, TPS36 and TPS40, respectively) were prepared and melt blended with the LDPE as depicted in Figure 5. In order to evaluate the effect of PE and TPS viscosities on the morphology of LDPE/TPS blends two commercial LDPE resins, LDPE2040 (PE1, MFI = 12g/10min) and LDPE2049 (PE2, MFI = 20g/10min), and the three TPS were used.

4.1 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 Figure 6. PE1 blends prepared with TPS40 and TPS36 (Figures 6a and 6b) show a high level of deformation in the machine direction. Conversely, blends compounded with TPS29 show very little deformation (Figure 6c) and even less when prepared with PE2 (Figure 6d). The singular morphologies displayed by PE/TPS blends are closely related to the differences in viscosity of both TPS and PE. As mentioned in section 3, it was found that 30% glycerol is required to effectively plasticize starch (Rodriguez-Gonzalez et al., 2004). From Figure 6, 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 Low-viscosity PE2 is used, it can be seen (Figure 6d) that the dispersed particles of TPS are of a spherical nature and that the particle size has increased compared to those of PE2/TPS29 blends (Figure 6c). 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.

4.2 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 (Figure 7). 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 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 (Figure 8). 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 Figure 8 that increasing the concentration of the TPS at low glycerol contents has little effect on the particle shape.
Fig. 6. 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.
Fig. 7. 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 10μm.

Fig. 8. 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 10μm.
Fig. 9. (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.
4.3 Mechanical properties

4.3.1 Elongation at break (ε_b)

The relative elongation at break (ε_b/ε_b0) in the machine direction of PE1/TPS blends is shown in Figure 9a. 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 (St. Pierre et al., 1997), 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 Figure 9a. 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 into a LDPE matrix, which impeded proper water removal. The presence of water at the blending temperature (150°C) can lead to the formation of bubbles in the extrudate, which weakens the final product (Verhoogt et al., 1995). In the present system, water was completely devolatilized from TPS before mixing with polyethylene (Favis et al., 2003).

4.3.2 Young’s modulus

The relative Young’s modulus (E/E_0) is demonstrated in Figure 9b. Once again the results are excellent. The 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 (Leclair and Favis, 1996). 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.

4.4 Connectivity of TPS particles

4.4.1 Hydrolytic degradation of LDPE/TPS blends

It is well known that acid hydrolysis of starch involves the random cleavage of glycoside bonds producing from oligosaccharides fractions to glucose units (Leach, 1984). In order to quantitatively determine the extent of continuity of TPS blends, samples were exposed to hydrolytic extraction. Figure 10 shows the percent continuity of starch as a function of TPS content for PE1/TPS40 and PE2/TPS40 blends. In both cases there is a monotonic increase in continuity as the concentration of TPS increases. At concentration of 43% or lower, blend
morphology plays an important role on percent continuity of LDPE/TPS40 blends. Blends depicting elongated particles show higher percent continuity at comparative concentrations than those displaying spherical morphology. For instance, PE1/TPS40 blends containing 32% TPS40 have 66% continuity while PE2/TPS40 blends composing of 31% TPS40 have only 38% continuity. Above 50% TPS40, at almost 95% continuity, blend morphology does not make any significant difference. At 62 wt% TPS40 the percent continuity of starch domains reaches 100% and the starch phase could be completely extracted. This is indicative of the full connectivity of starch particles through the entirely sample (Figure 10). The use of hydrolytic degradation as previous technique to biodegradation studies could be an important tool to predict enzymatic and bacterial biodegradation.

Fig. 10. Accessibility of starch domains LDPE/TPS40 blends exposed in solution of HCl 6N for 72 hours.

4.4.2 Enzymatic degradation of LDPE/TPS40 blends

Numerous studies have been done to investigate the enzymatic hydrolysis of starch-based materials. These works involve blends system with synthetic polymers like LDPE (Danjaji, 2002), ethylene vinyl acetate (EVA) (Simons & Thomas, 1995; Araujo et al., 2004) and polycaprolactone (PCL) (Seretoudi et al., 2002). The kinetic of enzymatic degradation of TPS40 and LDPE/TPS40 blends is shown in Figure 11. Amylase from the enzymatic cocktail triggers the cleavage of 1-4 acetal link while glucoamylase attacks the 1-6 links of
amylopectin (Chaplin & Kenedy, 1986), which results in starch solubilization and, consequently, weight loss. The extent of enzymatic degradation of starch is depended on TPS40 concentration. As expected, raw TPS40 is completely degraded during the first 36 hours. Blends of PE1/TPS40 having 62% and 32% and PE2/TPS40 (69:31) result in weight losses of TPS40 of 97%, 65% and 32%, respectively at 72 hours. Therefore, weight loss percent is related to the total amount of TPS40 in the blends. Percolation theory is concerned with the connectivity of one component (in our case, TPS40) randomly dispersed in another (Peanaski et al., 1991). Peanansky showed that below an apparent percolation threshold of 30% by volume (40 wt%) of granular starch, only small amounts were accessible for removal. Granular starches are compact particles, such as those observed in the PE2/TPS40 blends. Fiber-like particles observed in PE1/TPS40 blends could be responsible for a lower apparent percolation threshold in this system and, consequently, higher enzymatic degradation values (Li et al., 2005). Extent of enzymatic degradation of LDPE/TPS40 blends is very similar to that obtained by acid hydrolysis.

![Graph](Image)

**Fig. 11.** Enzymatic degradation kinetic expressed as weight loss for raw TPS40 (●), PE1/TPS40 blends: (■) 62 wt % TPS40, (▲) 32 wt % TPS40 and PE2/TPS40 blends with (△) 31 wt % TPS40 as a function of incubation time.

On the other hand, TPS40 enzymatic degradation rate is depended on starch concentration and the accessibility of starch domains as is in the case of LDPE/TPS40 blends. TPS40 is almost insoluble in cold water. When TPS40 is exposed to cold water, it swells and glycerol...
and low molecular fractions become soluble, but the specimen shape remains intact. Enzymatic hydrolysis of insoluble polymers is known to be affected by the mode of interaction between the enzymes and the polymeric chains and typically involves four steps: (i) enzyme diffusion from the bulk solution to the solid surface, (ii) enzyme adsorption on the substrate, resulting in the formation of enzyme-substrate complex, (iii) catalysis of the hydrolysis reaction, and (iv) diffusion of the hydrolyzed fraction from the solid substrate to the solution (Azevedo et al., 2003). Blends with high loadings of TPS40 show an enzymatic degradation rate as fast as that of the raw TPS40 during the first 3 hours of exposure. This is probably due to the large amount of TPS40 observed on the surface of LDPE/TPS40 blends. Similarly, blends containing about 30% of TPS40 have less starch available on the surface and, consequently, the initial enzymatic degradation rate is slower than the others. As the soluble degradation products of TPS40 diffuse out of the sample, the number of active enzyme units available for starch degradation decreases resulting in a reduction of degradation rate. TPS40 is completely degraded in 36 hours, whereas PE1/TPS40 having 62% and 32% TPS40 and PE2/TPS40 compounded with 31% TPS40 reach their maximum degradation in 72 hours. Conversely, the 69:31 PE2/TPS40 stabilizes at a short period of about 20 hours, whereas the 68:32 PE1/TPS40 blends reaches its plateau at 48 hours. This is likely due to the connectivity of PE2/TPS40 (69:31) blend of starch from the surface; therefore the path of the enzyme is less obstructive.

4.4.3 Microbial biodegradation

Weight loss as a function of time is the most useful method employed to monitor biodegradation (Swanson et al., 2003; Bikiaris et al., 1997b). Figure 12 shows the weight loss of LDPE/TPS40 blends exposed to activated sludge as a function of degradation time. As expected, raw PE1 remains unchanged after 45 days. On the contrary, raw TPS40 is completely consumed within 21 days of exposure. For the LDPE/TPS40 blends, the maximum biodegradation extent is observed at times longer than the raw TPS40. If TPS40 particles are present only on the surface, and not interconnected with particles inside the LDPE/TPS40 blends, then it could be expected that starch domains would be completely biodegraded like the raw TPS40. Percent continuity observed in Figure 10 shows that TPS40 particles are interconnected one to another. At TPS40 concentration of about 30%, interconnection increases when the morphology of starch domains changes from spherical (PE2/TPS40 blend) to fiber-like particles (PE1/TPS40 blend). The extent of biodegradation of TPS40 at 45 days of extraction for PE1/TPS40 blends at 62%, 32% of TPS40 and PE2/TPS40 (69:31) were 92%, 39% and 22%, respectively. However, when the maximum biological extraction is compared with the maximum enzymatic degradation, important difference is noticeable, especially in blends with ca. 30 wt% TPS40.

Kinetic of biodegradation of TPS40 and LDPE/TPS40 blends shows two stages (Table 1). In all cases, there is a fast weight loss during the first 1.5 days, followed by another stage where biodegradation rate decreases progressively. The fast stage could be related to the combined effect of biodegradation and diffusion of glycerol and low molecular starch fractions out of the sample. Diffusion of water soluble components can be accelerated by starch swelling, as observed in raw TPS40, during the first 6 hr. Weight loss during this period is almost 4 times faster than the following 30 hr. In the case of LDPE/TPS40 blends,
starch swelling is limited by polyethylene matrix, which results in longer diffusion time. Decrease of biodegradation rate observed after 3 days could be explained by the lower degradability of TPS40 domains that remain in the material.

From comparison of the three degradation techniques, it can be inferred that some phenomenon is taking place during the bacterial degradation of LDPE/TPS40 blends. Weight losses for acid hydrolysis and biodegradation were 100% and 92%, 66% and 39%, and 38% and 22%, respectively for PE1/TPS40 (38:62), PE1/TPS40 (68:32), and PE2/TPS40 (69:31). In the case of PE1/TPS40 (38:62), the difference can be neglected due to the possibility of bacterial waste accumulation inside polyethylene cavities. At around 30% TPS40, however, differences are more prominent. This could be related to other phenomena. Micrographs of the surface of PE1/TPS40 and PE2/TPS40 blends (reported elsewhere) show that pores on PE1 matrix left after TPS40 extraction are below 1 μm, while those observed on PE2 ranged between 3 to 10 μm (Tena-Salcido et al., 2008). On the other hand, different microorganisms have a length between 0.4 and 14 μm and width of 0.2 to 12 μm (Gibbon, 1997). In the case of blends having about 30% TPS40, it is possible that microorganisms or their colonies can restrict starch diffusion by obstructing the polyethylene pores to result in a significant reduction of the final extent of biodegradation.

Fig. 12. Bacterial biodegradation kinetic expressed as weight loss for TPS40 (●), PE1/TPS40 blends with: (■) 62 wt% TPS40, (▲) 32 wt% TPS40 and PE2/TPS40 blends (△) 31 wt% TPS40 during exposure in activated sludge.
Table 1. Biodegradation rate for TPS40 and LDPE/TPS40 blends as a function of exposure time in activated sludge.

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<th>PE2/TPS40 (69:31)</th>
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<td>1.1</td>
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</tr>
<tr>
<td>30</td>
<td>0.3</td>
<td>1.0</td>
<td>0.5</td>
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</tr>
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</table>

5. Conclusions

The analysis of thermal properties of water-free TPS materials prepared in a TSE showed that granular starch was completely disrupted and that TPS shows a thermal transition below room temperature corresponding to the glass transition temperature and this Tg is dependent on glycerol content. As was observed for the thermal properties, the rheological properties were also highly dependent on glycerol content. η of TPS36 at shear rate ~ 130 s⁻¹ decreases by 20% when the glycerol content is increased from 36 to 40%. In the same way, G' and G” also decrease as glycerol content increases. However, a particularly dramatic variation is observed when the glycerol content is varied from 29 to 33%. These latter results suggest a phase inversion from a hard elastic network matrix to a soft amorphous one. The glycerol plasticization threshold thus occurs at a content of approximately 30%. This result concerning a critical plasticization threshold is very important for morphology control strategies.

The PE/TPS blends prepared using the one-step process demonstrated 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. 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.

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.
In this work, a relationship between morphology and biodegradation of LDPE/TPS blends was discussed. Percent continuity of the blends is monitored by means of hydrolytic degradation, from which the results show that at TPS concentration below 50%, it is depended on LDPE viscosity and above that value it is independent. Enzymatic degradation is a technique that is closer to the actual biodegradation than acid hydrolysis but we have demonstrated both to have an excellent correlation. However, a correlation of these two techniques with bacterial biodegradation is difficult because of the accumulative deposit of bacteria through empty pores left by the loss of TPS. This difference is more pronounced for the two blends we investigated which contain ca. 30% TPS. In these two blends, the extent of bacterial biodegradation was 39% and 22%, respectively which are less than 60% of the available TPS, as demonstrated by hydrolytic degradation.

6. References


Thermoplastics can be used for various applications, which range from household articles to the aeronautic sector. This book, "Thermoplastic Elastomers", is comprised of nineteen chapters, written by specialized scientists dealing with physical and/or chemical modifications of thermoplastics and thermoplastic starch. Such studies will provide a great benefit to specialists in food, electric, telecommunication devices, and plastic industries. Each chapter provides a comprehensive introduction to a specific topic, with a survey of developments to date.

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