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Rheological and thermal properties of thermoplastic starch with high glycerol content

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Abstract

This work is part of a series of papers devoted to the study of LDPE/thermoplastic starch (TPS) blends. In those papers, a starch/glycerol/water suspension was fed to a twin-screw extruder (TSE) and a water-free TPS was prepared in the first half of the TSE. Molten LDPE was added via a single screw extruder added midway on the TSE and the latter half of the TSE was used to prepare the blend. This approach allows for the preparation of TPS with particularly high loadings of glycerol plasticizer. In this paper, the thermal and rheological properties of water-free TPS (glycerol content 29–40%) prepared in the first half of a TSE using the above approach was analyzed. DSC analysis reveals the presence of a glass transition temperature (T_g) below ambient temperature, which indicates the complete gelatinization of starch granules. The T_g decreases from -45.6 to -56.2 °C as glycerol content increases from 29 to 40%.

Rheological properties in the shear and oscillation mode were determined on-line from the TSE and by using two oscillatory rheometers, respectively. Time sweep measurements demonstrate that TPS has excellent thermal stability at 150 °C, but becomes unstable at temperatures above 180 °C. The studies indicate, however, that TPS stability is maintained for short time periods at temperatures up to 200 °C. These results are important since they indicate that the potential exists to prepare stable TPS materials at high temperature by maintaining short residence times during processing. The shear viscosity of TPS (at $\dot{\gamma} \sim 130\ \mathrm{s}^{-1}$) decreases by 20% when the glycerol content is increased from 36 to 40%. Similarly, G' and G'' decrease as glycerol content increases, with a particularly dramatic reduction around 30% glycerol. This suggests the percolation threshold of the well-plasticized glycerol-rich soft regions. These results concerning the plasticization of starch are critical for morphology control protocols. The shear and oscillation viscosities of TPS (40% glycerol, TPS40) were compared with that of LDPE. It is shown that TPS does not follow the Cox-Merz relation, whereas LDPE measured under similar conditions does. The viscosity ratio of the system TPS40/LDPE is greater than 1 if measured in the dynamic mode, while it is less than 1 if determined from steady shear viscosity values. These results are highly relevant considering the importance of viscosity ratio on the prediction of the morphology of immiscible polymer blends.

Keywords: Thermoplastic starch; Thermal properties; Rheological properties

1. Introduction

Extrusion of starch-based products is common in the food industry (Gomez & Aguilera, 1983, 1984). In the polymer field, interest in this biopolymer has been recently renewed due to its abundance, low-cost, biodegradability and the possibility of processing using conventional polymer processing equipment.

The physicochemical and rheological characteristics of extruded starch products have been studied from the point of view of both food (Baird & Labropoulos, 1982; Fletcher, McMaster, Richmond, & Smith, 1985; Gomez & Aguilera, 1983, 1984; Lai and Kokini, 1990, 1991; Senouci & Smith, 1988) and polymer science (Aichholzer & Fritz, 1998; Della Valle, Buleon, Carreau, Lavoie, & Vergnes, 1998; Della Valle, Vergnes, & Tayeb, 1992; Willett, Jasberg, & Swanson, 1995; Willett, Millard, & Jasberg, 1998). During extrusion, starch granules are exposed to high temperature and shear and undergo

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structural changes such as gelatinization, melting and fractionation. The ability to process starch and the resulting physical properties depend on the extent of structural changes of the starch. During gelatinization, starch molecules are released from the granule structure (Gomez & Aguilera). The addition of a plasticizer to gelatinized starch allows free starch molecules to behave in a similar fashion to common thermoplastic synthetic polymers. Starch prepared in this fashion is known as thermoplastic starch (TPS).

TPS materials have been prepared with water (Kalichevsky, Jaroszkiewicz, Ablett, Blanshard, & Lillford, 1992) and other plasticizers such as glycerol (Arvanitoyannis & Biliaderis, 1999; Forssell, Mikkilä, Moates, & Parker, 1997; Lourdin, Bizot, & Colonna, 1997; Lourdin, Coignard, Bizot, & Colonna, 1997; Van Soest, Benes, & de Wit, 1996; Van Soest, de Wit, & Vliegenthart, 1996), sugars (Arvanitoyannis & Biliaderis; Kalichevsky, Jaroszkiewicz, & Blanshard, 1993) and other organics (Lourdin, Bizot et al.; Lourdin, Coignard et al.). The thermal properties of such materials have been evaluated using different techniques including DSC, DMTA and NMR. The evaluation of the role of plasticizer content on the thermal transitions of TPS materials has been complicated by the presence of more than one plasticizer, generally water and glycerol or sugars (Van Soest, Benes et al.). Another complication in those evaluations could be the high concentrations of the second plasticizer (above 20%) due to phase separation of starch-based materials (Arvanitoyannis & Biliaderis; Colonna et al., 1997; Kalichevsky & Blanshard, 1993). Colonna and co-workers found two thermal transitions for TPS materials at 25–30% glycerol (Colonna et al.). The low temperature transition (ca. −40 °C) was attributed to glycerol α-relaxation and starch β-relaxation. Kalichevsky et al. have also reported a substantial degree of phase separation at high plasticizer content in amylopectin–sugar mixtures (Kalichevsky et al.). In that work, they compared two processes for the preparation of TPS films (cast film and compression molding) and found that some differences in the concentration dependence of thermal transitions could be attributed to the mixing history.

The viscosity of TPS has been studied directly during the extrusion process using capillary and slit dies attached to the processing device (Aichholzer & Fritz, 1998; Della Valle et al., 1992; Fletcher et al., 1985; Lai & Kokini, 1990; Senouci & Smith, 1988; Willett et al., 1995; Willett et al., 1998). Most of those studies evaluated TPS viscosity using water or water/glycerol mixtures as plasticizer for starch resulting in the formation of bubbles at the exit of the die (Aichholzer & Fritz; Fletcher et al.; Willett et al.) at temperatures higher than 130 °C for low moisture extrudates and at 100 °C for materials having a moisture content of 30% (Willett et al.).

Recently, rotational rheometry has been used to advance the understanding of the viscoelastic behavior of starch-based materials in the melt (Della Valle et al., 1998; Dus & Kokini, 1990; Redl, Morel, Bonicel, Guilbert, & Vergnes, 1999; Ruch & Fritz, 2000). As with many other biopolymers (Ross-Murphy, 1995), TPS has been found to display a gel-like viscoelastic behavior (Conde-Petit & Escher, 1995; Della Valle et al.; Ruch & Fritz, 2000). Such rheological behavior has been related to the formation of a crystalline elastic network produced by the complexation of amylose molecules with lipids (Conde-Petit & Escher; Della Valle et al.) and the physical entanglement of starch chains caused by its very high molecular weight (Ruch & Fritz). Advancing the knowledge of the rheological properties of TPS, such as its viscosity and elasticity, in the melt is necessary in order to evaluate the performance of polymer–polymer blends with TPS. These properties are important parameters for the prediction of the phase inversion region and co-continuity of TPS/thermoplastic polymer mixtures (Bourry & Favis, 1998a,b; Metelkin & Blekht, 1984; Paul & Barlow, 1980; Utracki, 1991).

This paper takes advantage of previous work from this laboratory (Favis, Rodriguez-Gonzalez, & Ramsay, 2003; Rodriguez-Gonzalez, Ramsay, & Favis, 2003a) which allows for the preparation of a virtually water-free TPS with high loadings of glycerol plasticizer. The purpose of this work is to undertake a detailed examination of the influence of the glycerol content, as sole plasticizer, and operating temperature on the thermal and rheological properties of water-free thermoplastic starch. A detailed examination of the rheology under both shear and dynamic conditions is carried out. Since our previous work has centered on polyethylene/thermoplastic starch blends, some comparison to polyethylene rheology is also carried out.

2. Experimental

2.1. Materials

An LDPE resin (LDPE2040, referred to as PE1) from Rexene Chemical Co. was used as a reference for the rheological properties of TPS. Wheat starch (Supergell 1203-C) was kindly supplied by ADM/Ogilvie. This starch is composed of 25% amylose and 75% amylopectin. The original moisture content was around 7.1%. The glycerol was obtained from SIMCO Chemical Products Inc. and contained about 5% water as determined by refractive index measurements. Starch, glycerol and distilled water were mixed to form the suspensions used in the melt blending experiments. The water content of glycerol was considered in the calculations of the proportions of the suspensions listed in Table 1.

Table 1
Proportions used for the preparation of the starch/glycerol/water suspensions

Code	Starch (%)	Glycerol (%)	Water (%)
TPS40	48	32	20
TPS36	48.5	27.5	24
TPS33	49	24	27
TPS29	49.5	20	30.5

2.2. Thermoplastic starch (TPS) preparation

In previous work, PE1/TPS blends have been prepared in a one-step process using a co-rotating twin-screw extruder (TSE) and a single-screw extruder to feed molten LDPE (Favis et al., 2003; Rodriguez-Gonzalez et al., 2003a). In the above process, starch is gelatinized and plasticized in zones 1–4 of the TSE, then mixed with molten LDPE in zones 5–8. In this study in order to evaluate the characteristics of the pure TPS under similar conditions to melt blending, the TSE configuration was re-arranged to contain only zones 1–4 for starch gelatinization and plasticization followed by a pumping section (previous zone 8). The TPS materials were then extruded through a rectangular die to form ribbons having ca. 2 mm of thickness. TPS ribbons were cooled using a three-roll calendar at the minimal draw-ratio to avoid longitudinal orientation. This approach allowed us to prepare and characterize a TPS that was as close as possible to the state of the TPS at its point of contact with PE in the previous blending study. The processing temperatures in these zones were the same as those used in the LDPE/TPS blend preparation (Favis et al.). The screw speed was 150 rpm. The starch suspension was fed into the first zone of the extruder. Water used for gelatinization was almost entirely removed during the pass through the venting zone (Favis et al.). For that reason, this TPS can be considered as a binary system of starch and glycerol and, consequently, the glycerol content of the materials studied is 40, 36, 33 and 29% for TPS40, TPS36, TPS33 and TPS29, respectively.

2.3. On-line viscosity measurements

The TPS viscosity was measured directly from the TSE by replacing the rectangular die used for sample preparation with a series of capillary dies. Three capillary dies having the same diameter (0.328 cm) but different lengths were used. The *L/D* ratios of the capillary dies were 9.658, 15.491 and 23.183. 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 from this valve to avoid causing 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. The temperature of TPS was directly measured with a thermocouple, which was in contact with the molten polymer. Bagley's correction was performed using the pressure drop data from the three capillary dies. Power-law parameters were calculated by linear regression (Sigma Plot V.4.0 software, Chicago, IL).

2.4. DSC measurements

Samples were taken from TPS ribbons and conditioned for at least one week in a dessicator at 0% RH. The thermal properties were measured using a Differential Scanning Calorimeter Pyris 1 from Perkin–Elmer. Samples were heated and cooled at 10 °C min^{-1}. Glass transition temperatures (T_g) were scanned from −170 to 40 °C. Higher thermal transitions, such as fusion and crystallization, were scanned from 25 to 200 °C. The thermal transitions were calculated from the second heating cycle.

2.5. X-ray diffraction

X-ray diffraction analysis was performed in a Siemens D5000 diffractometer operating at 30 kV, 25 mA and over a scattering angle (2θ) range of 5°–30° at 0.6° min^{-1}.

2.6. Rheological measurements

Round samples (25 mm diameter) were cut directly from the TPS ribbons (around 2 mm thickness). Samples were dried in a dessicator for at least one week and maintained under these conditions until testing. The rheological properties were measured in the oscillation mode using two rheometers (a CSM Bohlin and an SR-5000 from Rheometrics). They were equipped with a 25-mm plate–plate configuration. All measurements were carried out under N_2 atmosphere. A seal of silicon grease was used to eliminate the evaporation of plasticizer, except in tests where the influence of plasticizer evaporation was examined. Tests devoted to the evaluation of the viscoelastic domain and of the thermal stability of TPS were carried out at a frequency of 1 Hz.

3. Results and discussion

3.1. TPS extrusion and on-line viscosity measurement

TPS extrudates did not present bubbles due to the almost complete 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 & Fritz, 1998; Della Valle et al., 1992; Lai & Kokini, 1990; Senouci & Smith, 1988; Willett et al., 1995, 1998), the viscosity (η) of both TPS and PE1 melts display

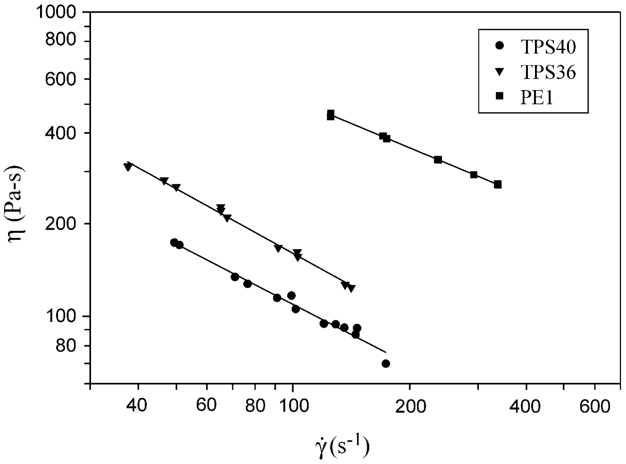

Fig. 1. Comparison of the viscosity of TPS40, TPS36 and PE1 measured on-line in the TSE at 150 °C.

a power-law (shear thinning) behavior at the shear rate ($\dot{\gamma}$) interval developed over die extrusion conditions (Fig. 1). The η of TPS materials depends on the plasticizer content. An increment of glycerol content from 36 to 40% results in a reduction of 20% of η of TPS36 (at $\dot{\gamma}$–130 s^{-1}). At the same $\dot{\gamma}$, the viscosity ratio between PE1 and both TPS36 and TPS40 was around 4 and 5, respectively. The Power-law index (m) and consistency (K) of TPS melts were calculated from the data in Fig. 1 and are listed in Table 2. The reduction of the TPS consistency has been attributed to the plasticizing effect of glycerol (Aichholzer & Fritz; Della Valle et al.; Lai & Kokini, 1990; Willett et al.). Nevertheless, there are discrepancies in the changes in power-law index. There is a decrease of m as glycerol content increases, similar to that found in a study of the extrusion of waxy maize (Lai & Kokini, 1990). During the study of the shear viscosity of cornstarch, Willett et al. found that m varies slightly at different water contents (Willett et al.). However, an important decrease of m was observed when the content of certain co-plasticizers was increased. In a further work, Willett and co-workers reported that m increases as the water content of waxy maize increases (Willett et al.). The relationship between m and the plasticizer content is quite complex and depends on a number of parameters such as processing history, plasticizer type, and the presence of other additives.

Table 2
Power-law parameters for TPS40, TPS36 and LDPE2040

Code	Consistency K (Pa s^{m})	Power law index m	Correlation coefficient
TPS40	2275	0.659	0.978
TPS36	4140	0.705	0.994
PE1	5957	0.531	0.999

3.2. Thermal properties of TPS

Knowledge of the structural changes produced by melt processing and of the effect of additives on thermal transitions is necessary for the prediction of the mechanical and rheological behavior of starch-based materials. Techniques such as DSC, DMTA, X-ray diffraction and NMR have been used to evaluate structural changes (Della Valle et al., 1998; Kalichevsky et al., 1993; Lourdin, Bizot et al., 1997; Lourdin, Coignard et al., 1997; Van Soest & Borger, 1997). Slade and Levine (1987) used a fringed micelle model to describe the partial crystallinity of native starch. In that model, starch is conceptualized as a three-dimensional network composed of microcrystalline regions that behave as physical cross-linking points for an amorphous matrix (Slade, Levine, & Finley, 1988). Three characteristic thermal transitions may exist for such semi-crystalline polymers: a glass transition for the amorphous fraction (T_g), a thermal transition for the melting of crystallites (T_m) and a transition due to crystallization (T_c).

As mentioned earlier, TPS materials prepared in this work are almost water-free starch–glycerol systems (Rodriguez-Gonzalez et al., 2003a). Compared with other studies, 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 (Fig. 2). On the other hand, no thermal transitions are observed between 25 and 200 °C (not shown). The T_g of TPS decreases from -45 to -56 °C as glycerol content increases from 29 to 40%. Van Soest et al. have reported the T_g of extruded TPS materials containing a starch/water/glycerol ratio of 100:27:5 of $\approx +59$ °C (Van Soest, Benes et al., 1996; Van Soest, de Wit et al., 1996). Forssell et al. studied the thermal transition of TPS materials prepared in a melt mixer as a function of glycerol and water content (Forssell, Mikkilä, Moates, & Parker, 1997). 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 ≈ -50 °C. The upper transition was attributed to starch-rich phase while the lower transition was related to a starch-poor phase. Lourdin and co-workers prepared TPS cast films by mixing starch with different amounts of water and glycerol (Lourdin, Bizot et al., 1997; Lourdin, Coignard et al., 1997). Films having around 13% water content showed a reduction of T_g from 90 to 0 °C when glycerol content increased from 0 to 24% (Lourdin, Bizot et al.; Lourdin, Coignard et al.). In that case they observed a glassy to rubbery transition of TPS at around 15% glycerol. In a further paper, they compared the T_g of TPS films having around 11% water with respect to

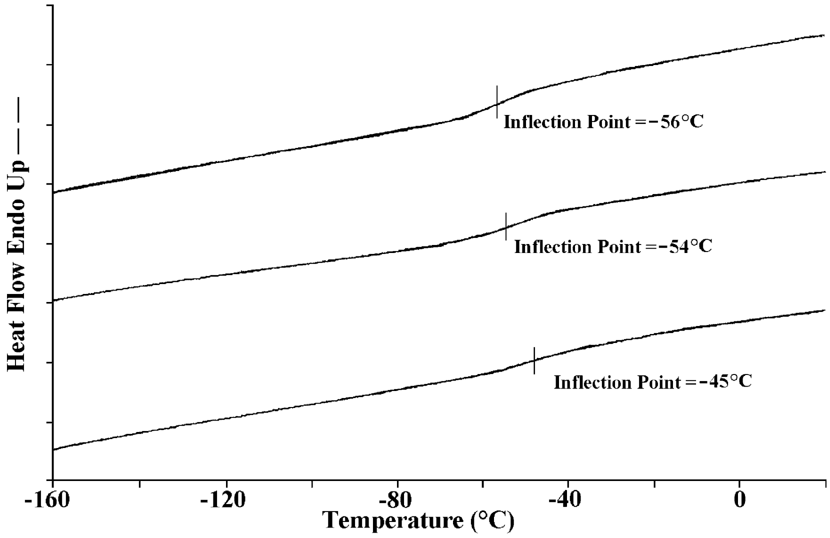

Fig. 2. DSC thermograms of TPS samples conditioned for 24 h at 0% RH. The glycerol content in TPS is 40, 36 and 29% from the top to the bottom.

glycerol content and they found that T_g decreased from 126 to 28 °C when glycerol content was increased from 0 to 40% (Lourdin, Bizot et al.; Lourdin, Coignard et al.). Discrepancies in T_g 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).

Disruption of the crystalline region, such as that which occurs during starch gelatinization (Donovan, 1979), leads to the disappearance of thermal transitions above T_g. However, in this work, X-ray diffraction shows the presence of crystalline regions (Fig. 3). Other authors have observed the same signs of ordered regions in glycerol-plasticized wheat starch (Della Valle et al., 1998). Those peaks have been related to the presence of lipids in wheat starch granules, which have the ability to form complexes with amylose. The size of starch crystalline domains in TPS can typically be in the order of 15–30 Å. And the DSC is likely not sensitive enough to detect the presence of such small crystalline regions formed by amylose–lipid complexes.

3.3. Thermal stability

TPS is found to be highly stable at 150 °C (Fig. 4) with only a slight reduction (ca. 2.33%) in complex modulus (G^*) after almost 2 h. On the other hand, TPS becomes unstable at 180 and 200 °C. A reduction of 10% of the complex modulus of TPS was observed at 25.5 min at 180 °C and after 11 min at 200 °C. Nevertheless, these data are very important since they indicate that blends of TPS and other polymers may be produced even at temperatures close to 200 °C, if short residence times are maintained. Our previous work has reported on a one-step processing technique for the blending of thermoplastic starch with synthetic polymers which allows for the possibility of very short residence times at high temperature (Bourry & Favis, 1998a,b; Favis et al., 2003).

3.4. Effect of plasticizer evaporation

The re-processing of LDPE/TPS blends (TPS with 40% glycerol) in a twin-screw extruder was examined in a recent paper from this laboratory (Rodriguez-Gonzalez et al., 2003b). The TPS particles of original blends showed an excellent elongational deformability while dispersed particles of re-processed blends were not able to deform. Reduced deformability of re-extruded TPS was related to glycerol evaporation during the pass through the vacuum venting zone at 150 °C. TGA measurements corroborated the possibility of glycerol evaporation at such low temperature. In order to evaluate the effect of glycerol evaporation on the rheological properties of TPS, experiments were carried out in the rheometer without the silicon grease seal.

Both the storage and loss modulus increase with time due to the evaporation of glycerol (Fig. 5). Although glycerol is lost only through the gap between the two plates, glycerol diffusion promoted by test shearing renews the plasticizer content in the outer surface.

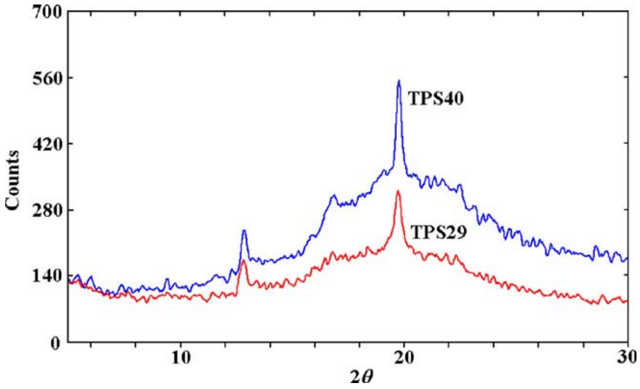

Fig. 3. X-ray diffraction patterns of extruded and dried TPS compounded with 29 and 40% glycerol.

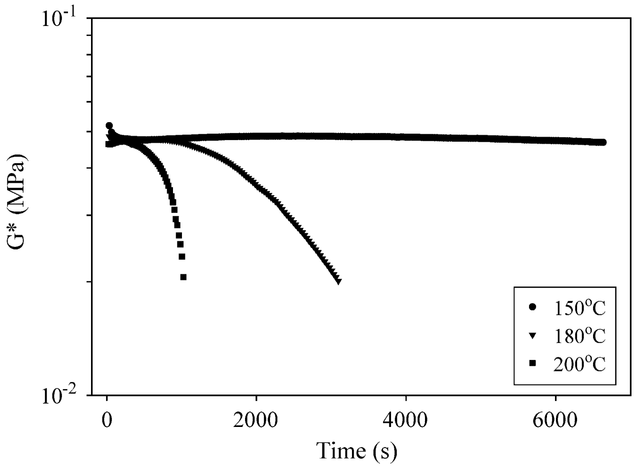

Fig. 4. Thermal stability of TPS40 evaluated at a frequency of 1 Hz and different temperatures.

3.5. *Effect of glycerol content*

TPS exhibits the rheological behavior of a typical gel as characterized by a storage modulus (G', Fig. 6a) larger than the loss modulus (G'', Fig. 6b) 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.; Ruch & 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 showed that the formation of amylose-emulsifier complexes modifies the viscoelastic response of potato starch dispersions (Conde-Petit & Escher, 1995). 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 Fig. 6a, 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. This statement was corroborated by the comparison of X-ray diffraction patterns between TPS40 and TPS29 (Fig. 3), where no change of the crystalline to amorphous fraction ratio occurs. It appears that crystalline regions created by the amylose–lipid complex are not uniquely responsible for the viscoelastic behavior shown by TPS material, even though it may be an important part of it.

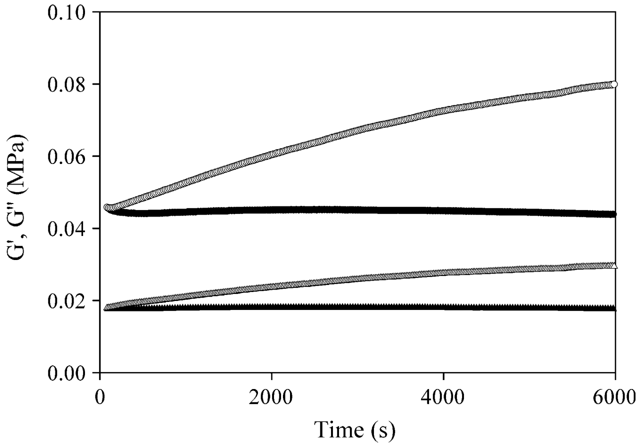

Fig. 5. Effect of plasticizer loss on G' (●, ○) and G'' (▲, △) of TPS40 at 150 °C and a frequency of 1 Hz. TPS40 was coated with (dark symbols) and without (light symbols) silicon grease.

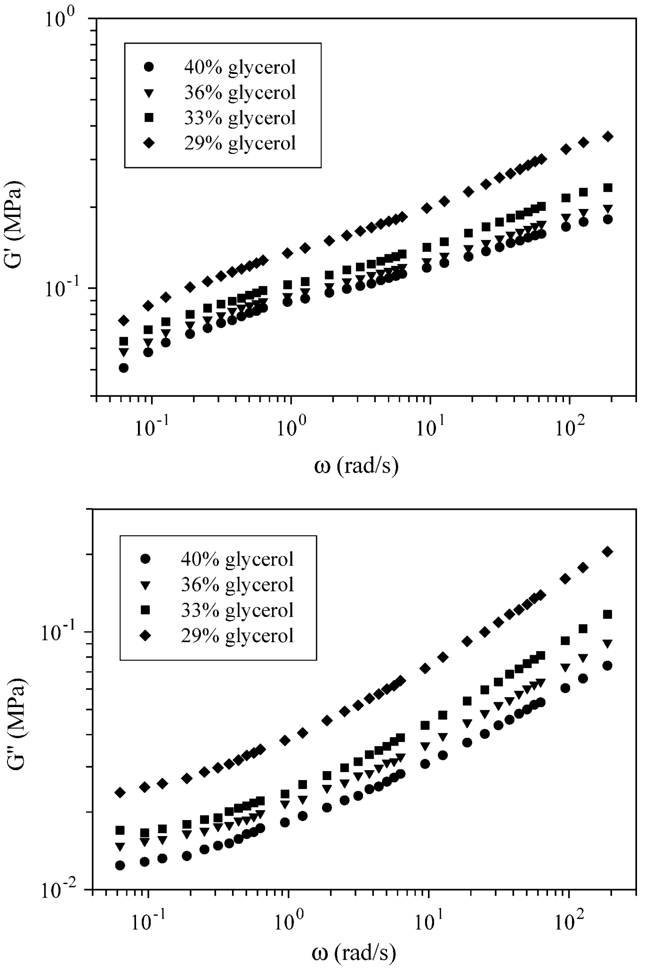

Fig. 6. Effect of glycerol content on (a) elastic modulus (G') and (b) loss modulus (G'') of TPS materials evaluated at 150 °C.

The study of the viscoelasticity of starch-based materials has mainly focused on concentrated gels and dispersions (≥5% starch). In this work, the viscoelastic behavior of almost 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). Fig. 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%. This result concerning a critical plasticization threshold is very important for morphology control strategies. A more in-depth study of starch microstructure is necessary to determine the actual components of the hard elastic network and the soft amorphous regions in TPS materials.

3.6. *Comparison of TPS viscosity measured in oscillation and shear modes*

The real component of the viscosity ($\eta' = G''/\omega$) of PE1 and TPS40 was compared with the respective values of η (Fig. 7). The results clearly indicate that TPS does not follow the Cox-Merz relation, whereas LDPE measured under similar conditions does. The Cox-Merz empirical relation states that at high shear rate/frequencies dynamic and shear viscosity should converge (Dus & Kokini, 1990). The trend observed in Fig. 1, where η of TPS $<$ η of PE1 is inverted in the case of η'. This is likely due to the higher molecular orientation exerted during extrusion through the capillary die. At lower shear, the intermolecular interactions have a more important effect on the rheological properties of TPS. This fact is extremely important considering that the rheological properties of TPS are fundamental for the theoretical prediction of the morphology of TPS-based blends. Under dynamic conditions, the viscosity ratio between TPS40/PE1 is greater than 1, while under steady shear conditions the viscosity ratio is less than 1.

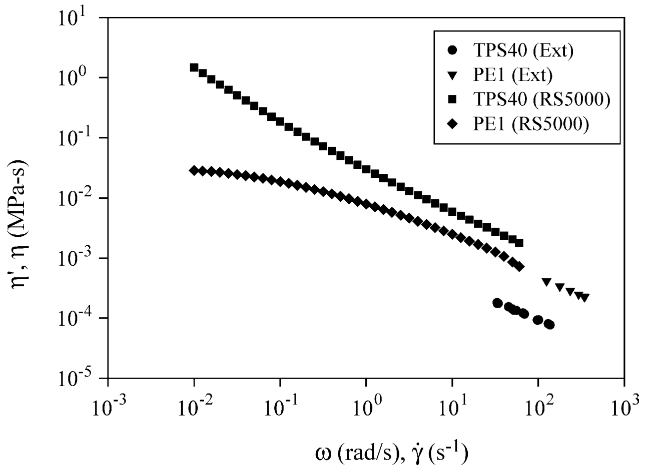

Fig. 7. Comparison of the viscosity (η') measured in the oscillation mode (RS5000 Rheometer) and the viscosity (η) of PE1 and TPS40 measured on-line in the TSE.

4. Conclusions

The study of the thermal transition of TPS demonstrates that granular starch was completely disrupted. The TPS shows a thermal transition below room temperature corresponding to the glass transition temperature and this T_g is dependent on glycerol content. Even though no thermal transition is observed above room temperature, a crystalline structure, which can be related to the complexation of amylose with lipids present in wheat starch granules, was detected by X-ray diffraction.

During rotational rheometry, TPS demonstrates an excellent thermal stability at 150 °C but becomes unstable at temperatures above 180 °C. The studies indicate, however, that TPS stability is maintained for short time periods for temperatures up to 200 °C. These results are important since they indicate that the potential exists to prepare stable TPS materials at high temperature by maintaining short residence times during processing. The evaporation of glycerol leads to a gradual increase in the rheological properties of TPS due to the stiffening of TPS.

As was observed for the thermal properties, the rheological properties were also highly dependent on glycerol content. The apparent viscosity of TPS 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.

Comparison of the shear and oscillation viscosity of TPS40 and LDPE show that TPS does not follow the Cox-Merz relationship while LDPE examined under identical conditions does. This result leads to important differences in the viscosity ratio for this polymer pair. Under shear conditions, LDPE is more viscous than TPS while in the oscillation mode the trend is reversed. These results are critical since morphology control strategies depend on an effective estimation of viscosity ratio in the blend system.

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