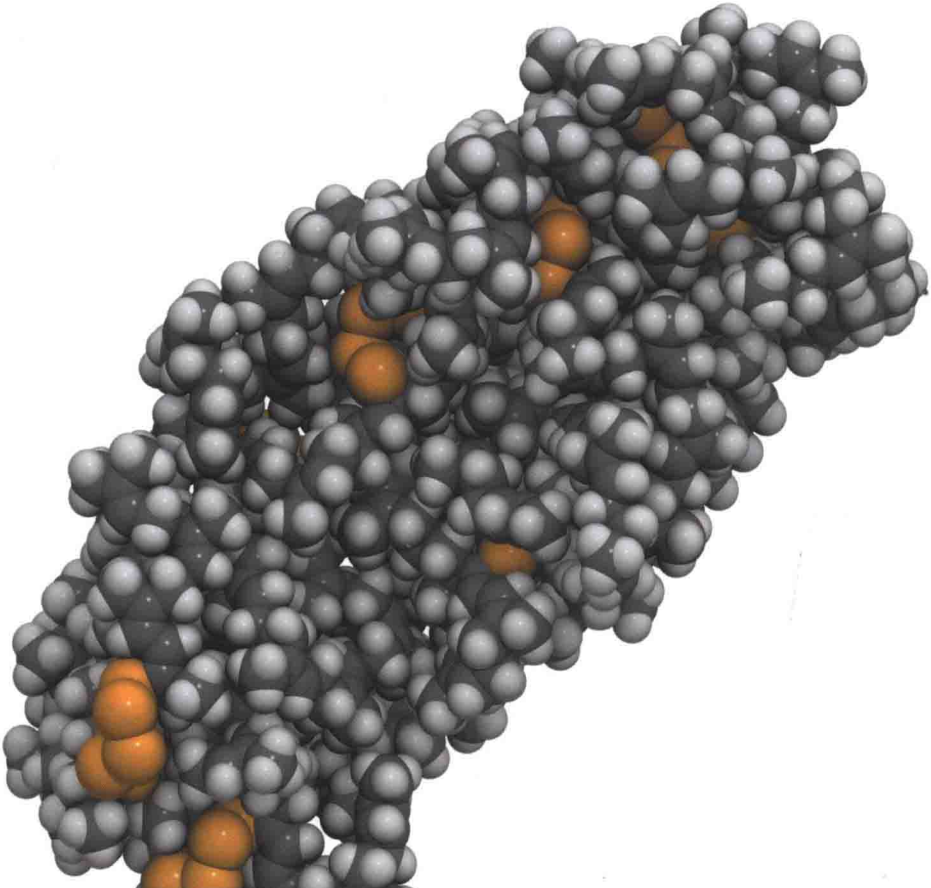
THERMOPLASTIC ELASTOMERS

Edited by **Adel Z. El-Sonbati**



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Preface

Nowadays it is difficult to imagine a life without thermoplastic elastomers. The uses of thermoplastic elastomers have increased because of its specific properties, such as low cost, light weight, high strength, non-biodegradability, durability, non-corrosive nature, process ability and high energy effectiveness. Hence, these thermoplastics elastomers can be used for various applications, which range from household articles to the aeronautic sector. This book is comprised of nineteen chapters, written by specialized scientists dealing with physical and/or chemical modifications of thermoplastic elastomers and thermoplastic starch. Such studies will provide a great benefit to the specialists in food, electric, telecommunication devices, and plastic industries.

The book "Thermoplastic Elastomers" is comprised of two sections.

Section I: Modifications of Thermoplastic Starch

The first section has seven Chapters on physical and/or chemical modifications of thermoplastic starch. Chapter 1 studies the relationship between morphology and biodegradation of thermoplastic starch blends.

Chapter 2 presents some excerpts related to thermoplastic cassava flour as a raw material useful for packaging applications. Cassava flour is viable material for use as part of a processable thermoplastic matrix by molding technique, which allows obtaining of materials with acceptable mechanical and thermal properties for agro-industrial applications.

The main starch modification obtained with the use of the thermoplastic extrusion process is addressed in Chapter 3. The thermoplastic extrusion process is capable of causing changes in starch, making it present a large variety of applications, both in the food industry and in other industries.

The modification of starch using various plasticizers, cross linking agent, as well as its biodegradation nature is discussed in Chapter 4.

Chapter 5 provides information on physical properties of starch foams such as cell structure, foam unit density and bulk density, compressive stress, resiliency and friability.

Chapter 6 provides a framework for transition from native starch, its primary molecular structure, secondary structure and tertiary granules to thermoplastic starch, with its properties that parallel and contrast with synthesis thermoplastics.

Chapter 7 summarizes the current knowledge of thermoplastic starch to its plasticization, retrogradation and antiplasticization. Starch retrogradation mechanisms are discussed at a molecular level. Methods to measure the retrogradation degree, such as differential scanning calorimetry, differential thermal analysis, X-ray, etc. are also reviewed. Changes in thermoplastic starch (TPS) property, such as tensile strength, elongation, gas permeability are due to the retrogradation of starch polymers and these are described.

Section II: Modifications of Thermoplastic Elastomers

The second section has twelve Chapters on physical and/or chemical modifications of thermoplastic elastomers. Chapter 8 compiles the updated knowledge on thermoplastic elastomers in general, practically their structures, syntheses, processing methods, mechanical properties and applications.

The subject of Chapter 9 observes a continuously growing interest in applications of reactive silanes and polysiloxanes in many different fields of material science and the chemical technology.

Chapter 10 shows the advantage of low interfacial adhesion thermoplastic matrix, such as polypropylene (PP), and how it can result in improvements to an aramid fabric for ballistics.

The challenges that involve the micro-injection of enhanced thermoplastics are discussed in Chapter 11. Special attention is given to the microinjection technology, tooling and injection materials.

The influence of some crucial production parameters, namely die air pressure, extruder pressure, collector drum speed, and collector vacuum on the thickness, basis weight, air permeability, fiber diameter and tensile properties of polypropylene meltblown nonwoven webs are investigated in Chapter 12.

Thermoplastic extrusion is considered a high-temperature, short-time (MTST) process in the food industry. The use of thermoplastic extrusion in food processing is studied in Chapter 13.

Lightweight plastic materials increasingly used in automotive, aerospace and construction sectors are studied in Chapter 14.

Thermoplastics demonstrating a track record of success in medical device applications are discussed in Chapter 15.

Application of thermoplastics in protection of nature fibers are described in Chapter 16.

Chapter 17 describes the characterization of thermoplastic elastomers by means of temperature scanning stress relaxation measurements.

Chapter 18 gives an overview of the research on ionic thermoplastic elastomers based on maleated ethylene propylene diene terpolymer (EPDM-g-MA), to obtain some new generations of ionic thermoplastic elastomers with high technical and processing characteristics, intended to be processed on the injection moulding machines, resulting in high quality products complying with the international market requirements.

Lastly, chapter 19 is about thermoplastic dielectric elastomers as a new generation polymer actuator with a high auction performance. Electroactive thermoplastic dielectric high actuation performance is owed to their ultra high electrostriction coefficients. Such big electrostriction coefficient was attributed to their ultra high density of the dielectric mismatched interfaces.

The editor of this book would like to express his gratitude to **Prof. M.A. Diab** and **Prof. A.A. El-Bindary,** Chemistry Department, Faculty of Science (Demiatta), Mansoura University, Demiatta, Egypt, for their useful advice in the process of preparing the book.

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Contents

Part 1

Modifications of Thermoplastic Starch

1

Melt Blending with Thermoplastic Starch

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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 be 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 processabillity. This material is known as thermoplastic starch (TPS).

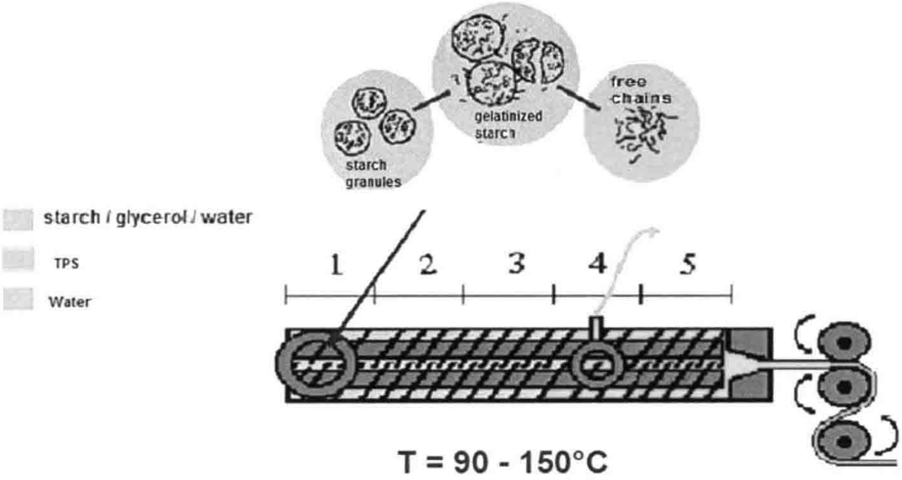

Fig. 1. Schematic representation of starch gelatinization and plasticization processes during extrusion.

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.

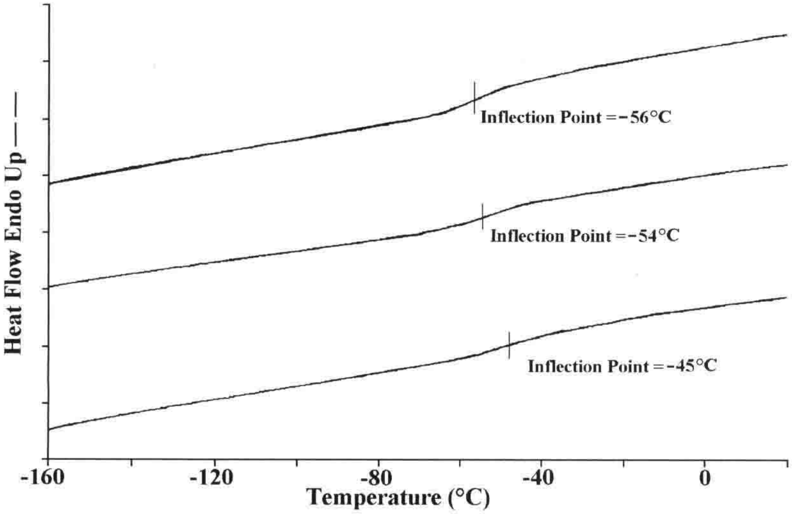

Fig. 2. DSC thermograms of TPS samples conditioned for 24h at 0% R.H. The glycerol content in TPS is 40, 36 and 29% from the top to the bottom.

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 ≈ -50°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 (η) 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 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}).

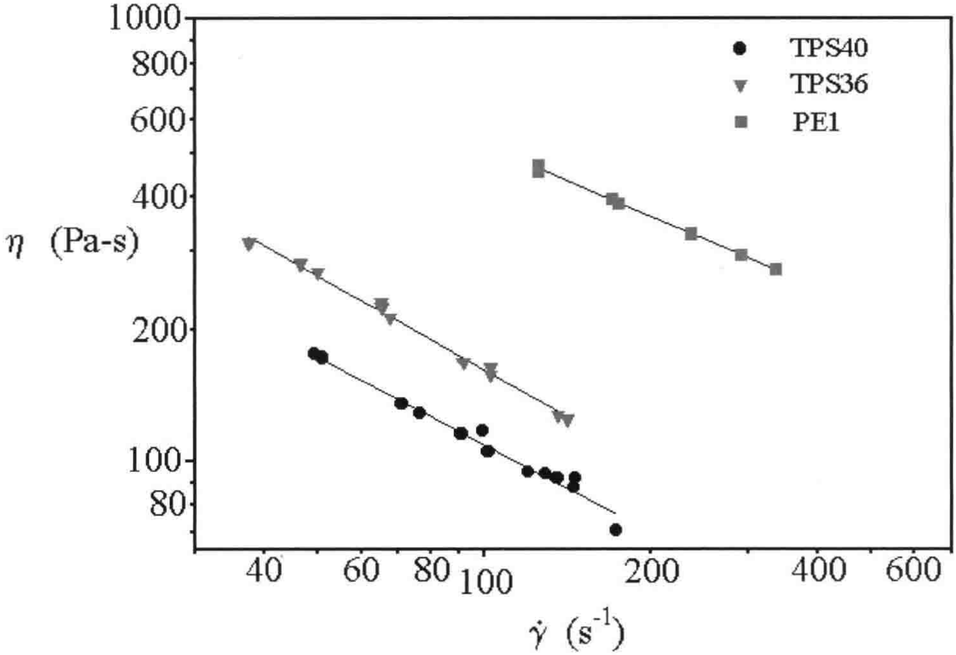

Fig. 3. Comparison of the viscosity of TPS40, TPS36 and PE1 measured on-line in the TSE at 150°C.

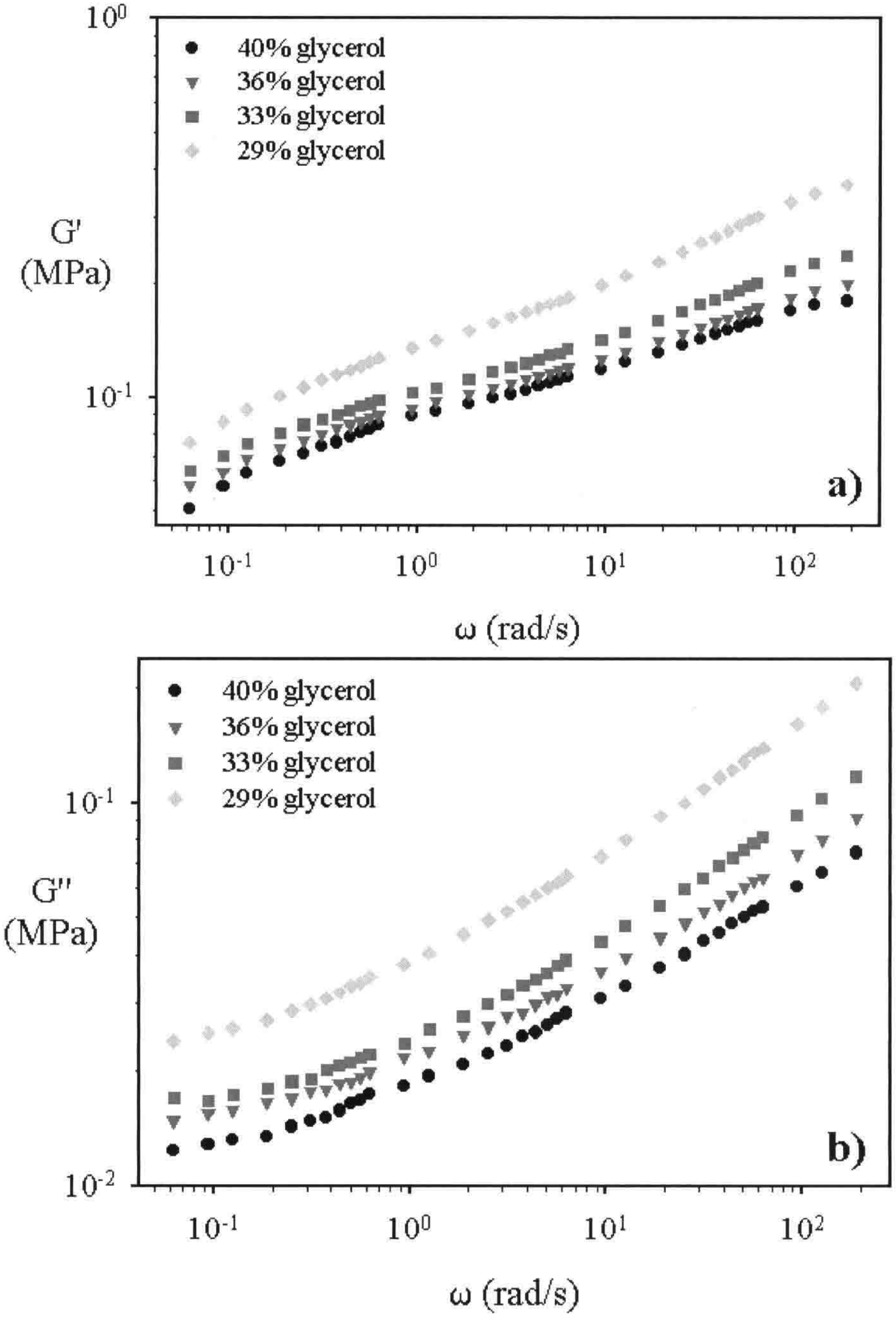

Fig. 4. Effect of glycerol content on (a) elastic modulus (G′) and (b) loss modulus (G″) of TPS materials evaluated at 150°C

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 (≤ 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%.