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The effect of plasticizers on thermoplastic starch compositions obtained by melt processing

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Abstract

The effect of the type and amount of plasticizer on the mechanical, thermal and water-absorption properties of melt-processed thermoplastic starch was investigated. In general, monohydroxyl alcohols and high molecular weight glycols failed to plasticize starch, whereas shorter glycols and sorbitol were effective. The quantity and type of plasticizer did not affect appreciably the crystallinity of the processed samples, but influenced the mechanical properties of these TPS in two opposite ways, viz. a softening effect due to the plasticizing of the amorphous phase and stiffening one due to an antiplasticization effect.

Keywords: Thermoplastic starch; Plasticizers; Crystallinity; Water affinity; Thermal and mechanical properties

1. Introduction

The possibility of transforming starch into a thermoplastic material (TPS) has spurred considerable interest in the last decade (Stepto, 2003; Roper, & Koch, 1990). The characteristics that make starch a promising substrate are its wide availability, its low cost and its renewable character. The investigation of new plasticizers and new processing techniques constitute major topics within this context (Lourdin, Coignard, Bizot, & Colonna, 1997; Poutanen, & Forssell, 1996; Mathew, & Dufresne, 2002).

The main plasticizer used in TPS compositions is glycerol (Stepto, 2003; Poutanen, & Forssell, 1996; Lourdin et al., 1997), but several other compounds, like ethylene glycol (Poutanen, & Forssell, 1996; Lourdin et al., 1997; Smits, Kruiskamp, Van Soest, & Vliegenthart, 2003), urea (Shogren, Swanson, & Thompson, 1992) as well as sorbitol and other sugars (Poutanen, & Forssell, 1996) have also been successfully employed. The proportion of plasticizer and its chemical nature influence strongly the physical properties of the processed starch in two ways, viz. (i) by controlling its destructuration and depolimerization and (ii) by affecting the final properties of the material, such as its glass transition temperature and modulus. Additionally, high plasticizer content TPS can exhibit phase separation as described by Lourdin et al. (1997) and these compositions were more sensitive to ambient humidity as the plasticizer content was increased.

In the majority of these studies, the plasticization is conducted in an aqueous medium and the compositions are obtained by casting the ensuing colloidal dispersions containing starch and the water soluble plasticizer. Of course, water has been known to play the role of starch plasticizer for a long time (Hulleman, Janssen, & Feil, 1998). However, melt processing seems to constitute a more realistic approach to the industrial preparation of TPS and several studies describe this approach (Shogren et al., 1992; Curvelo, Carvalho, & Agnelli, 2001; Bastioli, 1998).

The present investigation deals with the effect of a variety of potential plasticizers added to starch via melt processing in an intensive batch mixer and with the properties of the ensuing TPS.

2. Experimental

2.1. Materials

Conventional cornstarch containing 28% of amylose, kindly supplied by Corn Products Brazil, was the base material used in this study. Reagent grade 1-octanol, 1-hexanol, 1-dodecanol,

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1-octadecanol, 1,4-butanediol (BUT), 1,6-hexanediol, 2,5-hexanediol, glycerol, ethylene glycol (EG), propylene glycol (PG), diethyleneoxide glycol (DEG), triethyleneoxide glycol (TEG), ethylene glycol monometyl ether, D-sorbitol (SOR), poliethyleneoxide glycol (PEG) 300 and 600, polypropyleneoxide glycol (PPG) 3500 and stearic acid were used as received.

2.2. Thermoplastic starch

Starch and the selected plasticizer were pre-mixed in polyethylene bags until a homogeneous material was obtained. The mixtures were prepared at 150 °C in a Haake Rheomix 600 batch mixer equipped with roller rotors rotating at 60 rpm. The mixing time was fixed at 6 min. A small amount of stearic acid (0.5 wt%) was added as a processing agent. The processed samples were hot pressed at 160 °C into 1 and 2 mm thick plates.

2.3. Scanning electron microscopy (SEM)

A Leo scanning electron microscope was used to examine the morphology of fractured surfaces, prepared in liquid nitrogen.

2.4. X-ray diffraction

The samples were conditioned at 25 °C and 53% relative air humidity (RH) for 30 days before the measurements. Diffractograms were recorded on a Rigaku diffractometer. Scattered radiation was detected in the angular range of 3–40°(2θ) at a speed of 2°(2θ)/min. The extent of crystallinity was estimated by the height ratio between the diffraction peak (B type at 17° and V type at 19.5°) and the baseline of the diffractograms, as proposed by Hulleman, Kabisvaart, Jabssen, Feil and Vliegenthart (1999).

2.5. Differential scanning calorimetry (DSC)

Differential scanning calorimetry was performed with a Shimadzu TA-50WSI calorimeter calibrated with indium and zinc. An empty pan was used as a reference. Samples were cut from the plates in circular form and weighed accurately (20 mg) into aluminum pans. Measurements were carried out under a nitrogen flow, from 25 to 300 °C, at a heating rate of 10 °C/min.

2.6. Tensile tests

The tensile tests were performed with an Instron 5500R Universal Test instrument, equipped with a load cell of 500 kg. The samples, previously conditioned at 53% of relative humidity between 23 and 26 °C for 30 days, were tested according to the ASTM D638M type II norm, using a crosshead speed of 50 mm/min. At least 6 samples of each composition were tested and the average value where taken.

2.7. Dynamic mechanical analysis (DMA)

These tests were conducted with a DMA 2980 TA Instrument working in the tension mode at 1 Hz with a pre-load of 0.01 N (maximum deformation of 0.025, corresponding to amplitudes in the range of 8.0–12 μm). The temperature range was −100 to 200 °C, with measurements carried out in steps of 5 °C (stabilization time 30 s). The samples ($35\times5\times1$ mm) were cut from the hot-pressed molded plates. The DMA

Table 1
Composition and appearance of the plasticized TPS

Sample identification	Plasticizer content (%)	Characteristic of ensuring compounds	Visual and handling characteristics of pressed plates
EG	15	Homogeneous mass	Opaque and fragile
	20		Transparent and flexible
	30		Transparent and flexible
	40		Transparent and fragile
PG	15	Homogeneous mass	Transparent and flexible
	20		Opaque and fragile
	30		Transparent and flexible
	40	Heterogeneous, partially plasticized	–
BUT	15	Homogeneous mass	Transparent and flexible
	20		Opaque and flexible
	30	Un-plasticized in powder form	–
	40		–
DEG	15	Homogeneous mass	Transparent and fragile
	20	Homogeneous mass[a]	Transparent and flexible
	30	Un-plasticized in powder form	–
	40		–
SOR	15	Homogeneous mass	Transparent and flexible
	20		Transparent and flexible
	30	Homogeneous mass[a]	Transparent and flexible
	40	Un-plasticized in powder form	–

[a] With the presence of a certain amount of un-plasticized material.

was taken in duplicate and despite the nonconventional behavior observed the results were reproducible.

2.8. Water absorption

Water absorption experiments were conduced on specimens of circular shape obtained from the hot pressed plates of TPS, with 8 mm in diameter and 2 mm in thickness. Prior to the water absorption measurements, the samples were dried at 80 °C to constant weight. The samples were conditioned in hermetic containers at 25 + 2 °C with 43, 53 and 75% relative humidity, using saturated solutions of K_2CO_3, $Mg(NO_3)_2 \cdot 6H_2O$ and NaCl, respectively, following the ASTM E 104 norm. The amount of water absorbed by the samples was determined by weighing them periodically, until a constant weight was attained. The water uptake (W) was given by the relation

$$W(\%) = \frac{M_t - M_0}{M_0} \times 100 \tag{1}$$

where M_t is the weight at time t and M_0 the initial weight.

3. Results and discussion

3.1. Material preparation

In all experiments, the mixing time of 6 min was adequate, since in general the samples were completely destructured after 4 min. Longer periods led to some starch degradation, as suggested by the development of a light brown color.

Of all the additives tested, only ethylene glycol, propylene glycol, 1,4-butanediol, diethyleneoxide glycol and sorbitol were effective in the desestructuration and plasticization of starch, as shown in Table 1. Ethylene glycol was the most effective of these compounds. The remaining compounds, namely 1-hexanol, 1-octanol, 1-dodecanol, 1-octadecanol, 1,6-hexanediol, 2,5-hexanediol, ethylene glycol monometyl ether, poliethyleneoxide glycol (PEG) 300 and 600, polypropyleneoxide glycol (PPG) 3500 and a mixture of PEG/glycerol, did not plasticize starch by melt processing and formed instead a two-phase mixture. Triethyleneoxide glycol appeared to plasticize starch, but the ensuing plates were extremely brittle and could not be handled.

It appears that the destructuration of starch required a high solvating power, which was only attained with additives

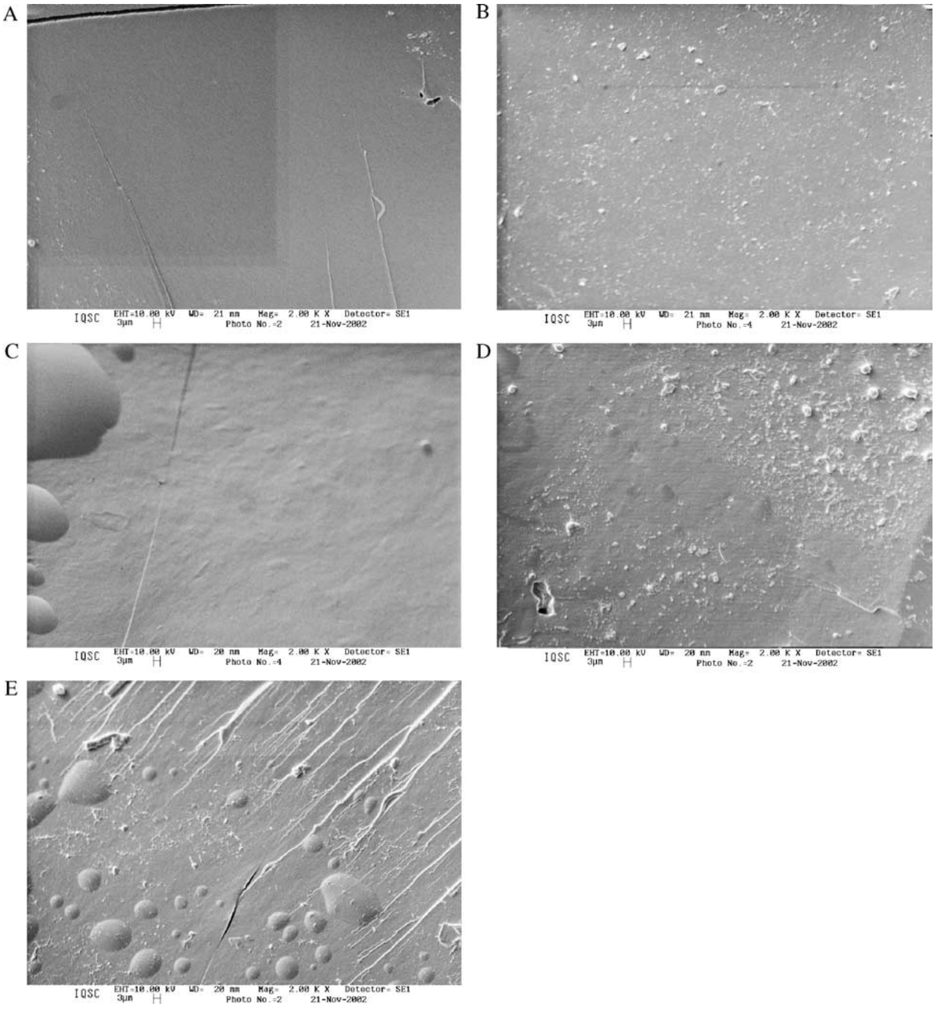

Fig. 1. SEM images of TPS plasticized with EG (A), PG (B), BUT (C), DEG (D)and SOR (E).

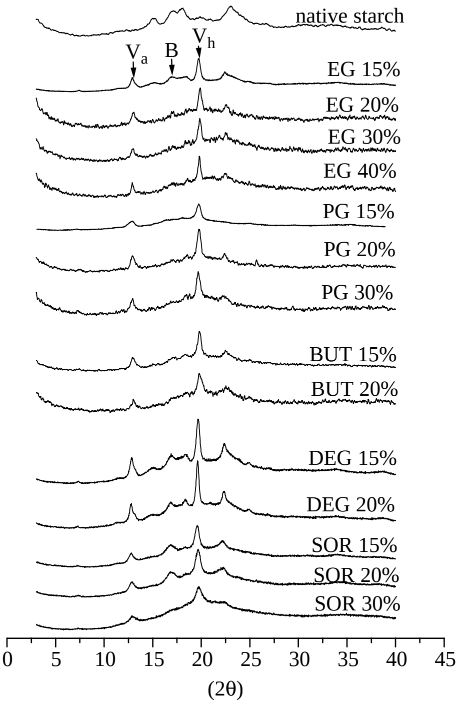

Fig. 2. X-ray diffraction patterns of native starch and plasticized TPS.

bearing a high proportion of hydroxyl groups within the molecular structure of the additive. Within the compounds tested in this study, the following general structure responds to the plasticizing criterion:

$$HO{-}\left[(CH_2{-}CHR)_n{-}O\right]_m{-}H$$

where n=1 or 2; m=1,2 or 3 and R=—H or CH_3.

The following sections only deal with the plasticized materials.

3.2. Morphological characterization

Visual observation of the plasticized TPS (plates obtained by hot pressing) showed that some compositions were clear and transparent, whereas others were opaque (see Table 1). The samples prepared with EG were the most homogeneous and transparent. TPS plasticized with PG and SOR were clear and transparent for the compositions with 15, 20 and 30%, while for 40% plasticization did not occur. Similarly, for BUT and DEG it was only possible to prepare samples with 15 and 20% of plasticizer, that were clear and transparent. One possible explanation for this, was that when plasticizer content was increased there was a strong decrease in melt viscosity, which made the plasticization of starch difficult, due to the decrease in the shear during processing.

The fragile fracture surface analysis obtained by SEM showed, in general, a smooth surface, typical of homogeneous amorphous materials, as shown in Fig. 1. Similar results have been reported for TPS, such as reported by Mathew and Dufresne (2002) for sorbitol and maltitol plasticized waxy maize.

3.3. X-ray diffraction analysis

Fig. 2 shows the X-ray diffractograms of the plasticized TPS samples compared with that of native starch. The original A-type crystallinity of starch was replaced by a B-type diffraction pattern (Van Soest, Hullenam, Wit, & Vliegenthart, 1996; Galliard, & Bowler, 1987) in the TPS. This morphological transition necessarily went through amorphous starch, formed during the processing, which recrystallized into the new form, as previously detected with glycerol (Van Soest, & Essers, 1997; Bastioli, 1998). The B and V peaks are indicated in Fig. 2 and were used for the calculations of the crystallinity index (Xc), which are given in Table 2.

In a general form the crystallinity of samples are almost independent on the compositions, except for EG and PG plasticized TPS for which the B and V_h crystallinity increased with their content. This increase was probably facilitated by the progressively higher chain mobility associated with the correspondingly higher plasticizer concentration.

Table 2
Quantitative characterization of the plasticized TPS

Sample identification	Plasticizer content (%)	tan δ (°C)	T_m (°C)	ΔH_m (J/g)	X_cB[a]	X_c V_h[a]	E (MPa)	σ_r (MPa)	ε_r (%)	Water uptake in equilibrium (%)		
										43RH	53 RH	75 RH
EG	15	45±1.0	160	–	0.73	0.88	63±8	1.1±0.4	10±2	2.8	6.1	10.5
	20	20±1.2	149	102	0.73	0.89	83±21	2.6±0.5	30±7	11.9	17.5	38.2
	30	10±1.1	142	107	0.83	0.94	126±23	3.3±0.5	47±7	15.7	22.7	50.2
	40	10±0.6	133	115	0.87	0.95	74±33	2.0±0.7	31±7	16.2	23.3	51.3
PG	15	4±0.6	104	73	0.67	0.87	90±14	3.2±0.5	36±3	2.7	10.9	11.5
	20	35±1.1	162	78	0.75	0.92	158±88	3.1±1.5	34±16	5.4	11.4	26.0
	30	25±0.9	130	100	0.80	0.94	202±36	3.7±0.9	38±8	11.1	17.2	40.0
BUT	15	5±0.8	153	104	0.76	0.92	147±87	3.3±0.8	32±23	2.7	13.5	14.7
	20	25±1.2	158	110	0.78	0.92	34±8	0.9±0.3	35±12	3.8	17.0	18.0
DEG	15	10±1.1	102	140	0.76	0.89	178±49	3.9±0.9	21±5	1.1	5.5	12.8
	20	30±0.9	108	144	0.76	0.91	54±11	1.7±0.2	23±3	1.5	5.9	13.3
SOR	15	15±1.0	172	–	0.72	0.85	219±15	4.8±0.8	28±8	≈0	0.5	5.6
	20	61±0.8	161	85	0.72	0.85	118±10	3.2±0.7	24±7	≈0	1.0	7.6
	30	77±0.9	151	97	0.68	0.84	59±7	1.1±0.3	10±3	0.5	2.5	11.4

[a] Non-conditioned samples.

3.4. Differential scanning calorimetry

The search for a clear-cut glass transition temperature feature in the DSC tracings was fruitless, as it often the case with starch and its derivatives. Therefore, no value of T_g is reported here. The melting transition appeared frequently as a large multiple peak. The mid-peak melting temperatures (T_m) and the corresponding heats of melting (ΔH_m) are presented in Table 2.

With EG and PG, ΔH_m was found to increase moderately with increasing plasticizer content, in agreement with the corresponding X-ray crystallinity data (Table 2). This trend was previously observed for glycerol- and EG-based TPS obtained by casting from water suspensions (Smits et al., 2003). With BUT and DEG, the increase in plasticizer content did not alter appreciably the extent of crystallinity, as suggested by both ΔH_m and X-ray data. With SOR, the trend was similar, but with larger scatter in the data.

3.5. Tensile tests

The stress–strain plots are shown in Fig. 3 and the corresponding data for modulus (E), tensile stress at rupture (σ_r) and strain at rupture (ε_r) are given in Table 2. The plots were linear at low strains showing high modulus values, thus displaying the typical behavior of semi-crystalline materials.

With EG- and PG-based TPS, the modulus increased with increasing plasticizer content, except for EG values

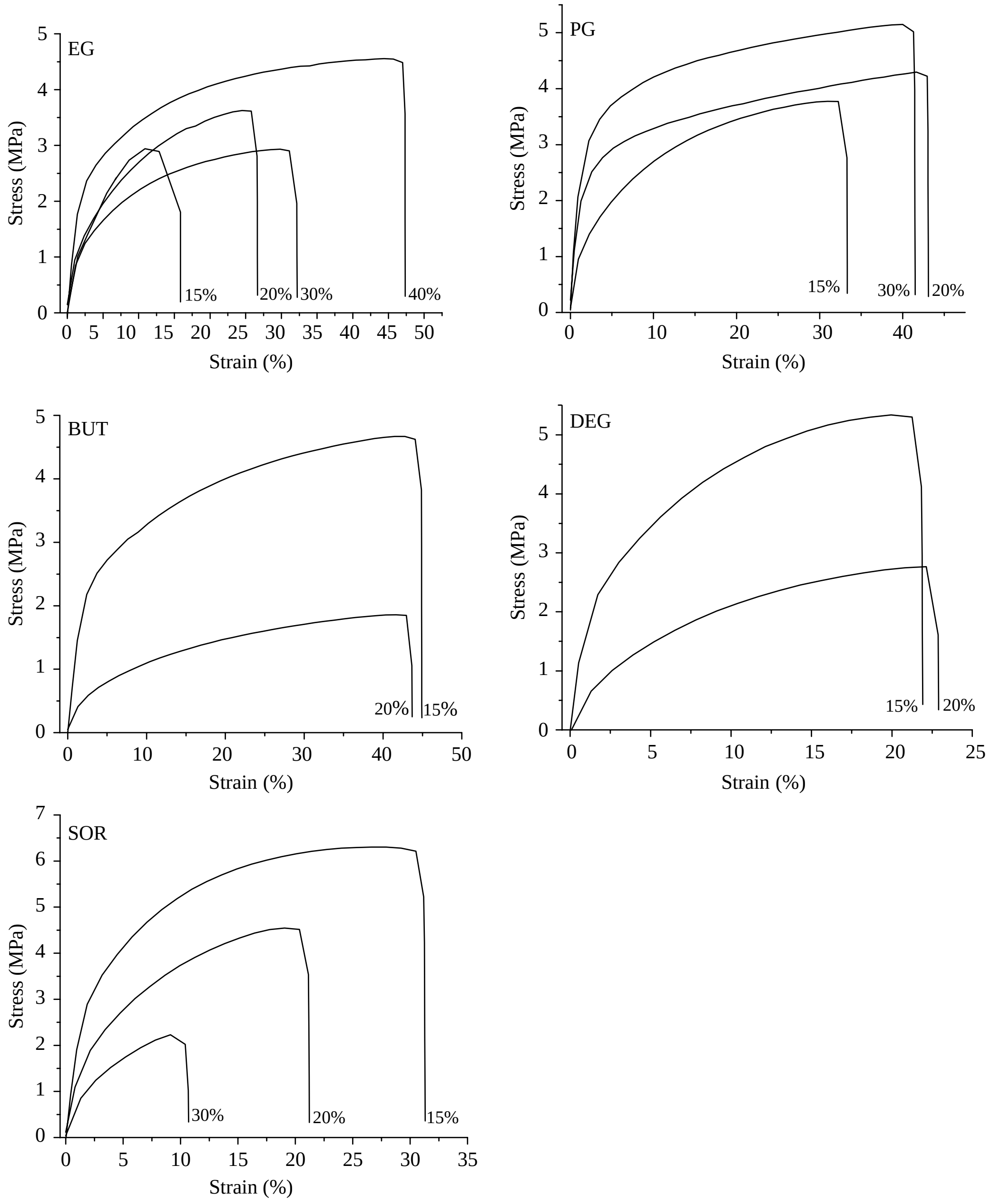

Fig. 3. Stress–strain curves of plasticized TPS.

above 30 wt%. Here, the modulus was affected in two opposite ways by the plasticizer, viz. (i) a decrease induced by plasticization and (ii) an increase caused by the corresponding increase in crystallinity. Given the trend observed with these plasticizers, it appears that the second effect prevailed for all these TPS, except with that containing 40% of EG, where the softening by plasticization (i) dominated over the increase in crystallinity (ii). Similar results were described previously for glycerol-based TPS (Lourdin, Bizot, & Colonna, 1997). With BUT, DEG and SOR, the modulus decreased as the plasticizer content increased, which suggests that for these TPS, the plasticization (i) prevailed.

3.6. Dynamic mechanical analysis

The variations of the storage modulus (E) and tan δ with temperature are plotted in Figs. 4 and 5, respectively. The tan δ peak temperatures are presented in Table 2. The tan δ curves for all the samples showed two relaxations, which appeared, respectively, between −75 and −40 °C and between 70 and 150 °C. The high temperature relaxation was attributed to the glass transition temperature of the corresponding TPS, whereas the low temperature peak could have arisen from a plasticizer-rich phase, as already suggested by other authors (Curvelo et al., 2001; Mathew, & Dufresne, 2002).

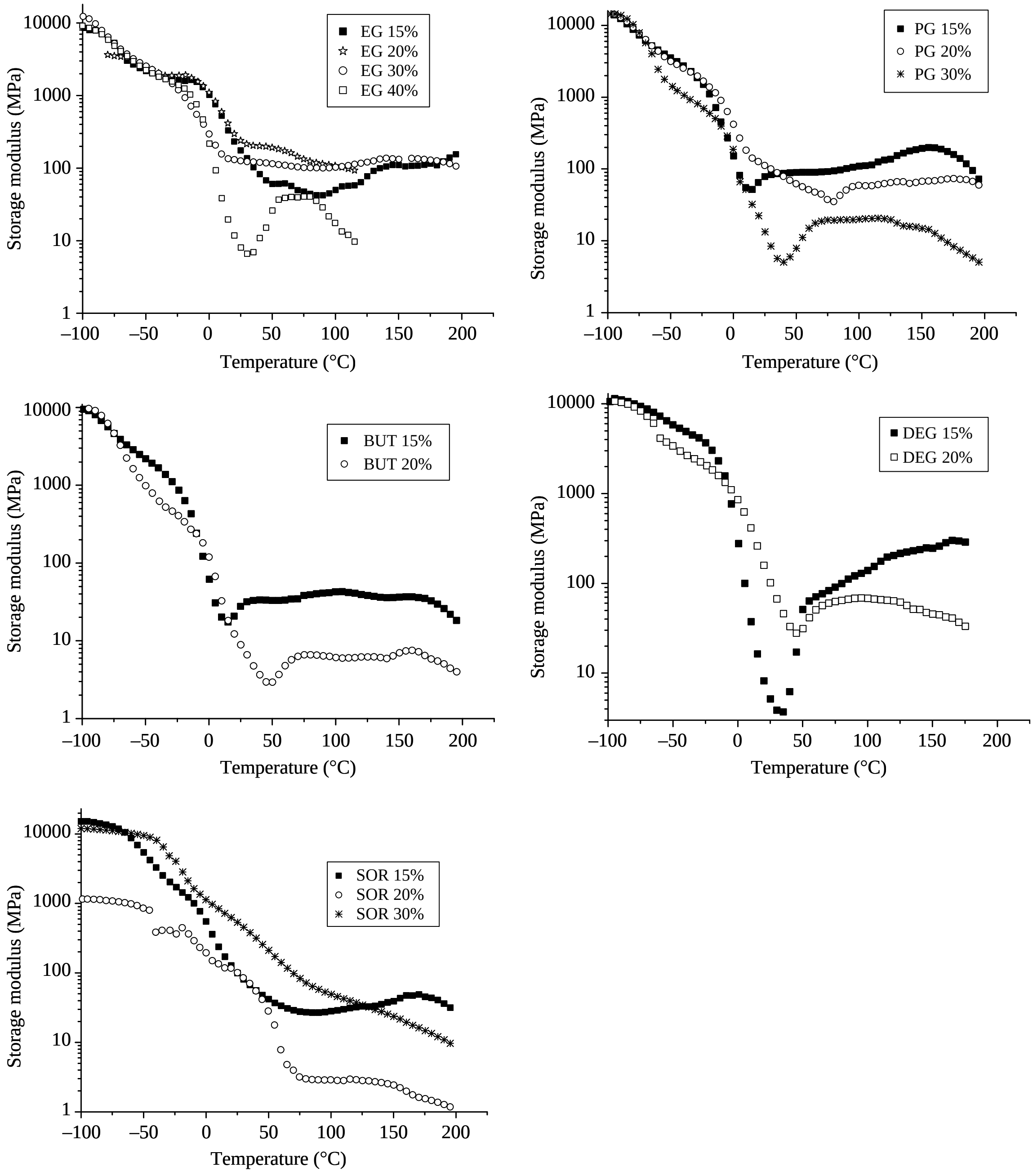

Fig. 4. Storage modulus versus temperature curves of plasticized TPS.

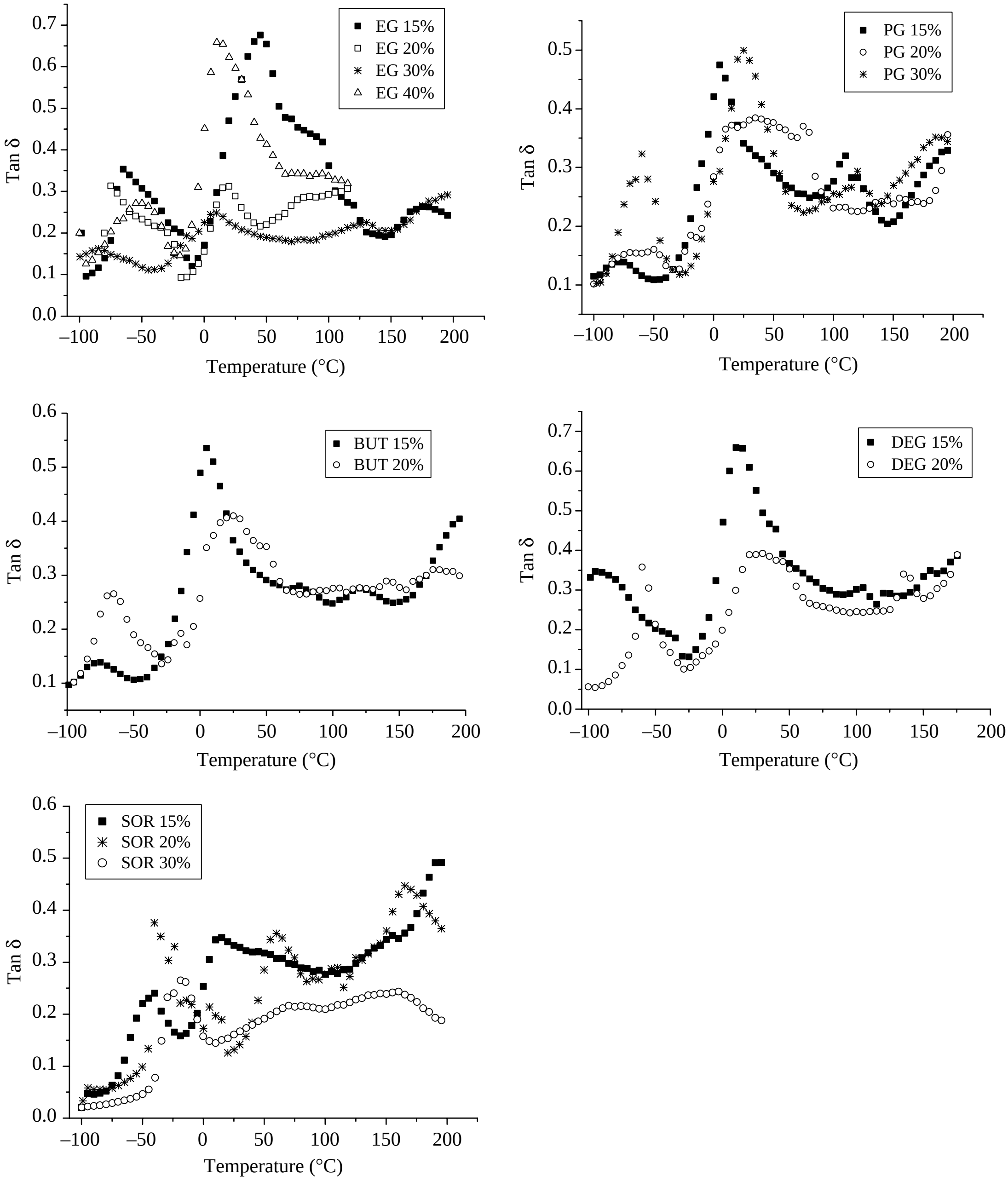

Fig. 5. tan δ versus temperature curves of plasticized TPS.

The tan δ peak temperatures, which can be assimilated in the first approximation to the corresponding glass transition temperatures, followed different trends, depending on the plasticizer used and on the amount added. The classical softening effect was only clearly detected with the EG-based TPS up to 30%. The reverse effect was encountered with BUT, DEG and SOR, which suggested the occurrence of anti-plasticizing features (Lourdin, Bizot, & Colonna, 1997; Sears, & Touchete, 1982). With PG, the behavior was less clear. The storage modulus for all materials after the glass transition temperature displayed a plateau typical of semi-crystalline polymers. Except for the samples with EG and SOR the plateau temperature decrease as the plasticizer content is increased. For EG TPS the modulus of the plateau was approximately independent on plasticizer content and for the TPS with SOR the modulus decreased from 15 to 20% of plasticizer and than increased for the 30% plasticized samples. This effect was attributed to an antplasticization effect.

3.7. Water absorption

The kinetics of water uptake displayed the typical increase with time until the equilibrium was reached. The data corresponding to the final water uptake are given in Table 2. As expected, these values increased with increasing atmospheric moisture content.

For all the samples, the equilibrium water uptake increased with plasticizer content as described by Shogren et al. (1992);

Loudin et al. (1997). However, the actual values for the four diols used here decreased as a function of their size, i.e. their OH molecular concentration. This trend is in tune with the observation concerning the plasticizing aptitude discussed above and could be interpreted as reflecting a progressive decrease in the hydrophilic character of the TPS. The fact that the SOR-based samples displayed an exceptionally poor water affinity, which goes against this conclusion, was rationalized in terms of specific hydrogen bonding interactions between its multiple hydroxyl groups and those of the starch macromolecules. This interpretation is corroborated by the strong antiplasticizing effect induced by SOR.

4. Conclusions

A thorough investigation of the plasticizing aptitude of numerous OH-containing compounds provided useful criteria on structure–plasticizer relationship. With the successful additives, the ensuing TPS, prepared by melt-processing, were characterized systematically and provided novel interesting materials.

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