"Antiplasticization" in Starch–Glycerol Films?

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ABSTRACT: Calorimetric, mechanical, and thermomechanical properties have been measured on starch films with various glycerol/water contents. For calorimetric measurements, a continuous decrease in T_g was observed as glycerol increases from 0 to 25%. Mechanical properties exhibit a minimum of elongation at break for glycerol content $\sim$ 12%. In slightly hydrated starch films not containing another plasticizer, a β relaxation is detected by DMTA around $-68°C$. This relaxation is modified by the presence of glycerol, the α relaxation of which appears in the same temperature range. Results are discussed comparing with the well-known antiplasticization effect in synthetic polymers such as PVC and PC. The combination of the plasticizer α mode and the polymer β mode is considered. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63**: 1047–1053, 1997

INTRODUCTION

The role of a plasticizer added to a polymer is to increase the suppleness (ductility) of the material (yield at break, ε) and improve its behavior in all types of stress mechanics, such as successive folds. Unfortunately, this effect cannot be dissociated from the weakening of the mechanical behavior of the material when subjected to a constraint (maximum stress, σ). From a thermodynamic point of view, this additive decreases glass transition temperature (T_g), for example, below the usual temperature for obtaining a rubbery material. On a molecular scale, this transition corresponds to cooperative translation motions of the main chain, such as the spreading of chains around junction zones or their entanglement (α-relaxation).[1]

Contrary to this orthodox behavior of plasticization, some polymers show an antiplasticization effect corresponding to a decrease of ε and an increase of σ when the additive is introduced in low amounts (generally <15%). This atypical but well-known behavior has been related to that of some polymer-additive compositions, such as PVC-dioctylphthalate[2] and PC-dibutylethylenedibenzoate[3,4] binary systems. Studies conducted by the Jackson group have shown that antiplasticizers are generally compatible with the polymer and contain polar heteroatoms such as halogens, nitrogens, oxygens, or sulfurs. These additives are often of small size (<5.5 nm) compared to monomeric units, and have an intrinsic $T_g > -50°C$. Polymers susceptible to antiplasticization have a high-modulus vitreous behavior, demonstrate glass transition at a relatively high temperature, and contain substituents or polar groups such as chloride in polyvinylchloride (PVC), or carbonyl in polycarbonate (PC), which are likely to produce marked interaction with the plasticizer. Glass transition temperatures for binary systems subject to an antiplasticization effect remain higher than ambient temperature. However, when the additive concentration is sufficiently high (generally >15%), the material recovers its rubbery behavior, manifesting a classic plasticization phenomenon.

Even though the phenomenon of antiplasticization has long been observed in synthetic polymers, the mechanisms involved are not perfectly known.

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Two relatively old hypotheses are still proposed and frequently confirmed. The first, derived from the work of Horsley,[2] relates the amount of crystallinity of the PVC-dioctylphthalate (DOP) system to the antiplasticization effect. X-ray measurements show a maximum level of crystallinity when plasticizer concentration is low in the material. The greater molecular mobility afforded by the plasticizer improves the reorganization of the material and, therefore, its crystallinity. With respect to mechanical properties, crystallinity greatly decreases the yield at break of the material by a physical crosslinking effect. This hypothesis, which has been confirmed for PVC,[5] does not define the general causes of the antiplasticization effect, since no increase in crystallinity has been shown for other polymers such as polycarbonate.[6,7]

A second hypothesis proposed by Ghersa[8] suggests that strong interactions occur between the polymer and the plasticizer, producing a "crosslinker" effect at low concentrations in addition to possible crystallization. Several studies[5,9,10] in support of this hypothesis relate this effect directly to the modulation of intensity of a secondary relaxation mode (β-relaxation) at a temperature below that of the main glass transition (α-relaxation), generally observed within a temperature range from -120 to $-50°C$. Determination of molecular mobility by nuclear magnetic resonance on other types of polymers[11] has allowed this relaxation to be attributed to motions less cooperative than α modes. In comparison with α mode, which concerns translational diffusion of the main chain, β relaxation involves groups or short chain segments. The corresponding motions are viewed as local rotations of side groups or crank shaft motions along the backbone. The hypothesis most often evoked to describe the antiplasticization effect is that these motions can be constricted or even totally prevented upon addition of a compound capable of establishing connections with these groups.[10,12,13] Changes in free volume, as determined by the difference between specific volume and occupied volume deduced from the volume of Van Der Waals, are decreased in this domain.[14] In these cases of antiplasticization, β-relaxation can totally disappear. Thus, this transition is extremely sensitive to the presence (albeit in low amounts) of monomers or solvent traces or even of low amounts of water if the polymer is absorbent.

Starch antiplasticization by water or glycerol is sometimes mentioned in the literature[15] but has not been studied in detail. The purpose of the present study was to investigate the enthalpic, mechanical, and thermomechanical properties of starch films as a function of the concentration (0–25%) of a water/glycerol plasticizer mix, with particular attention to low contents (0–15%).

EXPERIMENTAL

The potato starches used were a gift from Roquette Frères (Lestrem, France). Glycerol used as a plasticizer was obtained commercially (Merck) and had a purity of >99.5%.

Films were obtained by the casting method. Native starch was solubilized in a high-pressure reactor at 130°C for 20 min using a 4% suspension in ultrapure water with a precise quantity of glycerol. The procedure was performed under a nitrogen atmosphere to avoid the risk of degradation. The solution was evenly spread on a Teflon coated hot plate kept at 70°C until adhesion between the film and the plate disappeared and induced edge curling. A transparent film with a mean thickness of approximately 100 μm, and which contained about 10% water (dry basis), was obtained. Before testing, all films were stored for 48 h in an atmosphere controlled by a saturated sodium bromide solution (R.H. 57% at 25°C).

After storage, the water content of films was determined by the Karl-Fisher method, and glycerol content by high-performance liquid chromatography (HPLC). After heating, the sample ($\sim$ 15 mg) was washed in pure water (100 mL) under vigorous stirring to achieve complete diffusion of the glycerol in the solution. Glycerol was then determined by HPLC on an Acidex H^+ column at ambient temperature (elution by water at 0.6 mL/min, differential refractometer sensitivity 2$\times$).

Maximum stress (σ) and yield at break (ε) were measured on an Instron 1122 universal testing machine. After conditioning, six to eight samples were cut off each film according to the standard ASTM D 412 method. Their thickness, as measured by a micrometer, ranged from 30 to 60 μm; stretching speed was set to 2 mm/min.

Measurements of the glass transition temperatures of the plasticized films were performed by differential scanning calorimetry on a DSC 121 apparatus (Setaram France). Films were reduced to powder by a cryogrinder and stored at constant relative humidity before being placed in pressure-tight DSC cells ($\sim$ 80 mg of matter per cell). The

Table I Compositions in Dry Matter, Water, and Glycerol in g per 100 g of Different Films Studied by Calorimetry

Glycerol	Water	Polymer
0.0	12.8	87.2
9.6	11.4	79.0
18.4	13.4	68.2
21.8	14.0	64.2
24.2	15.4	60.4

calorimetric measurement procedure was similar for all samples regardless of composition. A first scanning was performed from −30 to +150°C to delete any thermal events which may have occurred during the preparation and storage of the samples. Rapid cooling (60°C/min) to −30°C allowed the thermoplastic starch to be frozen in the amorphous state. Measurement was performed during a second scanning at 3°C/min. Graphic determination of glass transition temperature was done according to the procedure recommended by Wunderlich.[16] For a polymer, $T_g^{1/2}$ corresponded to a half-variation in calorific capacity during transition ($T_g^{1/2}$). Tests performed in triplicate showed that variations were of the order of ±3°C.

Thermomechanical measurements were performed on a Dynamic Mechanical Thermal Analyser (DMTA MKIII, Polymer Lab, Loughborough, UK). Vibration frequency in tension mode was set at 1 Hz, solicitation amplitude at 16 μm, and the heating rate at 3°C/min. Films were coated with a silicone-based hydrophobic grease to limit dehydration during experiments above ambient temperature. It was determined that a thin coating of grease had no effect on thermomechanical properties. The method of Arvanitoyannis[17] was used to determine glass transition temperature by thermomechanical analysis. As indicated (see Fig. 4), $T_g^{1/2}$ may be defined as the midpoint between the onset of the drop in the storage modulus E' and the peak of tan $\delta = E''/E'$. The temperature difference between the tan δ peak and the drop in storage modulus ($\Delta E'$) gave the breadth of the glass transition region.

Powder X-ray diffractograms were determined according to the procedure of LeBail.[18]

RESULTS

Composition

The different glycerol and water contents relative to the total mass (% w/w) of films studied by calo-

rimetry are indicated in Table I. The values given for dry matters were deduced from concentrations of the other constituents.

For the storage time allowed, water content relative to total weight was 11.4% minimum for a glycerol content close to 10%. When plasticizer content was higher, hydration increased (>15% of water for 24% of plasticizer).

As films are very sensitive to aging, mechanical and thermomechanical experiments were conducted exactly 48 h after their preparation. However, as the casting method is not reproducible, the glycerol contents of films specially prepared for mechanical and thermomechanical measurements showed differences from those of films studied by calorimetry. These values are not reported here, but the relations between the different constituents were the same as those reported in Table I.

Mechanical Properties

Representative curves showing maximum stress σ and yield at break ε for different glycerol contents of casting films stored for 48 h at 57% H.R. are shown in Figure 1. For purposes of simplification, these results are presented only in terms of glycerol content.

Maximum stress σ decreased rapidly with increasing glycerol contents, from 44 MPa for film without plasticizer to approximately 3 MPa for film containing 24% glycerol. The effect was intensified for a concentration range of 12 to 17%.

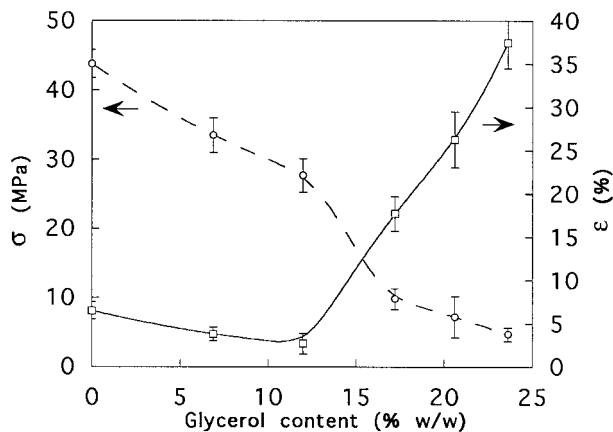For yield at break, two distinct forms of behavior were observed. When glycerol content was

Figure 1 Maximum stress (○) and yield at break (□) of potato starch films with different glycerol contents at 25°C.
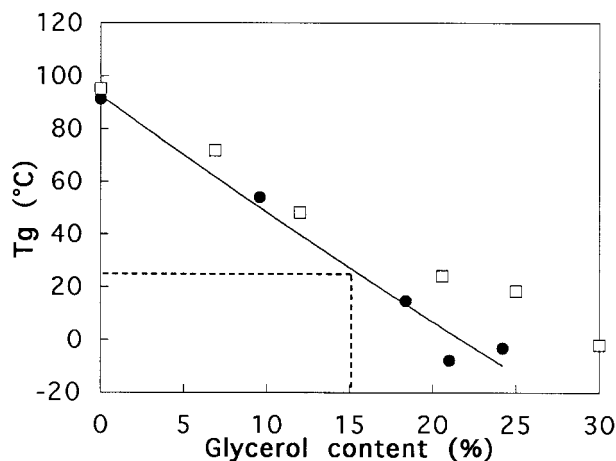
Figure 2   Variations of $T_g^{1/2}$ of potato starch films with glycerol content measured by DSC (●) and DMTA (□); 15% of glycerol content corresponds to T_g at ambient temperature (dotted line).

above 12%, the yield at break of materials increased markedly from approximately 3% to close to 40% of elongation. These changes as a function of glycerol content correspond to the classic mechanical behavior of a ductile polymer–plasticizer system. Conversely, when glycerol content was below 12%, there was an appreciable and unexpected decrease in elongation (from 7 to 3%) as plasticizer level increased.

X-Ray Spectra

X-ray measurements performed at the same time as the mechanical tests showed no crystalline structure.

Calorimetric Measurements

Glass transition temperature as a function of the glycerol content of thermoplastic starch was measured by DSC (Fig. 2). The lowering of T_g corresponded to the classic phenomenon of plasticization by dilution, at least for the lowest concentrations. T_g values did not seem to vary for the two higher plasticizer concentrations (21.8 and 24.2%). The curve fitted from calorimetric data was obtained using the Couchman equation[19] with a 13% approximation of constant water content. This corresponds to the limit between the rubbery domain (upper part of the graph), in which the material has the properties of a plastic solid (deformable), and the glassy domain in which the material is rigid. On the basis of this

curve, a glycerol amount of 15% can be extrapolated, which corresponds to a calorimetric T_g ~ 25°C (Fig. 2). A good correlation was obtained between the thermal values and the mechanical values described above: both types of measurements (Fig. 1) suggest that a plasticizer concentration close to 12% is required to obtain the brittle/ductile transition.

Thermomechanical Properties

The variations in tan δ and storage modulus E' of a starch film without glycerol (and only 12% water) are shown in Figure 3 as a function of temperature. A high peak appears at a temperature of ~ −68°C for a measurement frequency of 1 Hz. This event is apparently related to β relaxation and has been observed on amylose by several authors.[20–22] The temperature of β relaxation, which is known to be highly dependent on water content, corresponds to that reported by Bradley and Carr[20] for amylose films containing approximately 12% humidity.

Curves obtained by thermomechanical analysis of films containing 25 and 30% glycerol are shown in Figure 4. For these two formulations, as for all other films, two transitions, characterized by a maximum of the tan δ curve associated with a drop in storage modulus E', occurred at high ($T > 20$°C) and low ($T < -40$°C) temperatures.

At high temperature, the relaxation observed was markedly dependent on the plasticizer content of the material. The different (previously defined) $T_{g1/2}$ temperatures shown in Figure 2 may be compared with those obtained by calorimetric measurements. The results for the two techniques
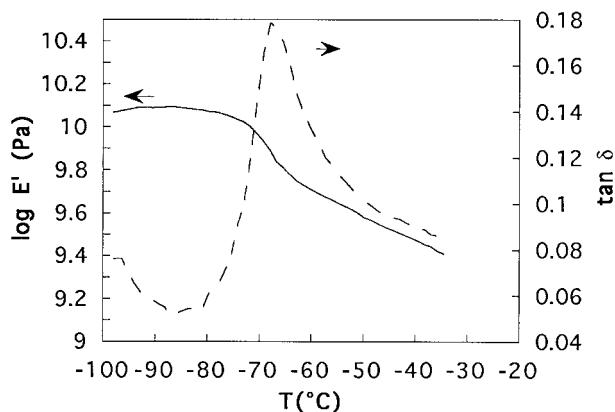

Figure 3   Storage modulus E' (—) and tan δ (− −) at low temperature for nonplasticized potato starch films (12% H_2O w/w).
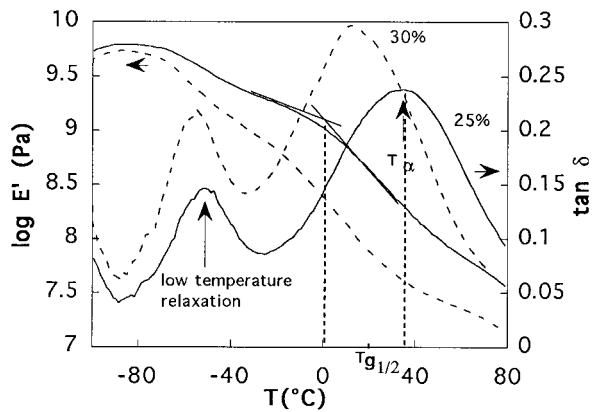
Figure 4 Storage modulus E' and tan δ for potato starch films plasticized by 25% (——) and 30% (– –) glycerol and $\sim$ 15% H_2O.

are similar for films with low plasticizer concentrations. The appreciable differences at higher concentrations are attributable to the existence of very broad T_g domains.

At temperatures of less than $-40°C$, another very intense transition not previously reported in the literature was apparent in samples containing glycerol. Figure 5 shows the tan δ curves for film plasticized only by water; three samples containing different glycerol contents are superimposed. For the formulation containing 12% glycerol, the quite intense β relaxation peak is replaced by a very flat peak over a large range of temperatures between approximately -80 and $-40°C$. For glycerol concentrations of 25 and 30%, the transition temperatures observed respectively at -52 and $-54°C$ seem to be only slightly dependent on plasticizer concentration. However, the temperatures increase with glycerol content. This observation suggests that this type of transition was due to the main plasticizer itself.

DISCUSSION

Several characteristics of thermoplastic starch studied in this work show similarities with the antiplasticization effects observed in synthetic polymers. Starch and glycerol contain many polar chemical functions, mainly hydroxyl groups. According to Jackson and Caldwell,[3,4] these characteristics can confer a certain susceptibility to antiplasticization on materials. Enthalpic measurements and associated mechanical properties have shown that a glycerol concentration of $\sim$ 12% is required to decrease glass transition below ambi-

ent temperature. When plasticizer content is higher, the increase in hydration of the quasi-liquid network is probably due to a better statistical accessibility to starch and glycerol sites since both substances are mobile. The measured mechanical properties are those of a supple plastic material. Glycerol and water play the role of internal lubricants, preventing the rigidification of non-crystallized macromolecular starch chains at ambient temperature.[22]

When there is less than 12% glycerol, the decrease in elongation reflects an unusual plasticization behavior, as in the case of PVC or PC, in which molecular mechanisms no longer involve glass transition, but, instead, one or more relaxations occur below ambient temperature. In fact, thermomechanical measurements indicate β relaxation in starch films without a plasticizer (other than water), such as synthetic polymers, similarly to synthetic polymers which are susceptible to antiplasticization. The molecular mechanisms implicated in this relaxation are poorly known and debatable. Some authors[20,21] have suggested that relaxation in this case corresponds to the rotation of the methylol groups of the glucose unit, whereas a more recent study by Scandola, Ceccorulli, and Pizzoli[23] proposes local movements of the main chain.

Although the study of pure glycerol does not seem possible by the Dynamic Mechanical Thermal Analyser, several reports have presented dielectric analyses concerning this product. In particular, Champeney and Kaddour[24] and Davidson and Cole[25] have demonstrated α relaxation of pure glycerol in a temperature range of -90 to
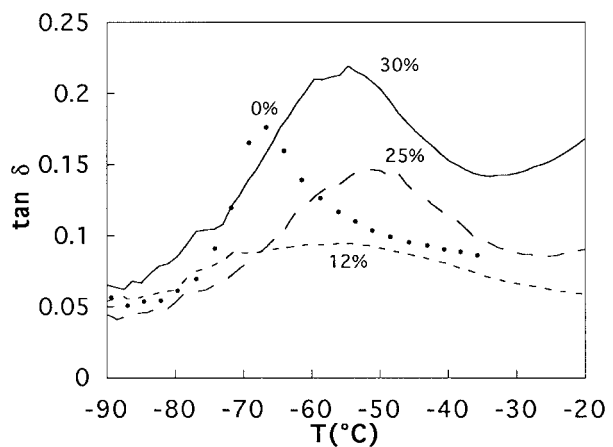

Figure 5 Low-temperature dynamic mechanical property (tan δ) for plasticized potato starch films with different glycerol contents and $\sim$ 13% water content.

−10°C for increasing frequencies in the applied field. For the binary water/glycerol system, calorimetric T_g has been found to range from −75 to −130°C with between 100 and 20% of glycerol.[26]

Two hypotheses can be formulated concerning the changes in starch β-relaxation in the presence of this plasticizer mix.

First, β-relaxation is inhibited by the presence of the plasticizer and the "new" transition is replaced at higher glycerol contents by the α-relaxation characteristic of this polyol. In this case, the mechanism involved is similar to that described for synthetic polymers, and the effect is in fact one of true antiplasticization.

Second, β-relaxation is shifted toward higher temperatures (reaching a maximum at about −53°C) by coupling with the α-relaxation of the water−glycerol mix. This hypothesis cannot be explained by the classic mechanism of antiplasticization.

In fact, several other results suggest that the term "antiplasticization" should be used with due caution in referring to starchy materials. For example, simultaneous variations in the two mechanical properties (increased σ, decreased ε) were not found for starch films. In antiplasticized synthetic polymers, the decreased yield at break was always accompanied by an increase in maximal stress and the modulus. In these materials, maximal stress, measured as a function of glycerol content, decreased continuously, even for low plasticizer concentrations.

Qualitatively, the antiplasticization mechanism proposed by Horsley,[2] involving macromolecular recrystallization, was not validated for plasticized starch. X-ray measurements of crystallinity levels showed no increase for low glycerol contents.

For starchy materials, multiple water−glycerol−starch interactions make the mechanisms involved much more complicated than those described in the introduction to this work. In this three-constituent system, the roles of the two competing plasticizers are dependent on their respective concentrations. For example, the precision assay of residual water revealed a minimum of adsorption in the "antiplasticization" concentration range, which is in agreement with the results of Guo.[27]

CONCLUSION

The glycerol content introduced into starch-based thermoplastic materials has a crucial influence on their properties at ambient temperature. When the amount of plasticizer exceeds 12%, the elongation behavior of films is "controlled" by glass transition, which involves the molecular motions described in different studies.[28,29] Below this "critical" concentration, some unusual properties present similarities to the antiplasticization effect found in synthetic polymers. The mechanisms that induce these properties at ambient temperature can only be understood by extending the study to include low temperatures at which one or more relaxations related to motions of small molecular groups are exhibited.

Knowledge and understanding of these effects are essential. Currently, all formulations of thermoplastic materials based on natural substrates require the use of very large amounts of plasticizers (roughly 20%) to avoid antiplasticization events. As a result, the materials have poor mechanical properties since the tiny molecule (or plasticizer) causes a relaxation of the polymer network. Thus, the very fine properties of pure amylose films, comparable to those of a classic thermoplastic polymer, are largely lost by the addition of 20 to 25% of glycerol.[30]

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