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Deformation mechanisms of plasticized starch materials

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ABSTRACT

The aim of this paper is to understand the influence of plasticizer and plasticizer amount on the mechanical and deformation behaviors of plasticized starch. Glycerol, sorbitol and mannitol have been used as plasticizers. After extrusion of the various samples, dynamic mechanical analyses and video-controlled tensile tests have been performed. It was found that the nature of plasticizer, its amount as well as the aging of the material has an impact on the involved deformation mechanism. The variations of volume deformation could be explained by an antiplasticization effect (low plasticizer amount), a phase-separation phenomenon (excess of plasticizer) and/or by the retrogradation of starch.

1. Introduction

The research on bio-based thermoplastics has to face several challenges for proposing credible alternatives to current commodity plastics (Belgacem & Gandini, 2008). Starch is a cheap, abundant and biodegradable natural polysaccharide that needs being plasticized for obtaining a thermoplastic material (Halley et al., 2008). Plasticization of starch needs a plasticizer, high temperature and shear force. Different plasticizers can be used as sorbitol (Gaudin, Lourdin, Forssell, & Colonna, 2000; Gaudin, Lourdin, Le Botlan, Ilari, & Colonna, 1999; Lourdin, 2003), maltose (Follain, Joly, Dole, Roge, & Mathlouthi, 2006; Lourdin, Ring, & Colonna, 1998), xylitol (Kirby, Clark, Parker, & Smith, 1993), glucose (Ollett, Parker, & Smith, 1991), ethylene-bis-formamide (Yang, Yu, & Ma, 2006a, 2006b) and glycerol (Follain et al., 2006; Godbillot, Dole, Joly, Rogé, & Mathlouthi, 2006; Kirby et al., 1993; Lourdin et al., 1998). Plasticized starch shows some drawbacks such as a high affinity for water, important properties variations with time and lower mechanical properties compared to synthetic polymers. However, the brittle behavior can be converted to a ductile behavior with a modulation of plasticizer amount or through the use of plasticizer blends (Mali, Sakanaka, Yamashita, & Grossmann, 2005).

The mechanical behavior of plasticized starches has been already evaluated (Chanvrier, Della Valle, & Lourdin, 2006; Jansson & Thuvander, 2004) but no study about their plastic deformation has been reported to date. Various techniques can be used for characterizing the plastic deformation mechanisms. Besides ultrasonic or acoustic emission techniques (De Rosa, Santulli, & Sarasini, 2009; Potel, Chotard, De Belleval, & Benzeggagh, 1997), the VideoTraction® method developed by G'Sell, Hiver, and Dahoun (2002) is based on the optical analysis of samples during the tensile test. This technique has been applied to study the plastic deformation of various polymeric materials such as classic thermoplastics (Addiego, Dahoun, G'Sell, & Hiver, 2006), biodegradable thermoplastics (Rezgui, Swistek, Hiver, G'Sell, & Sadoun, 2005) and more complex structures as fiber-reinforced composites (Bouaziz, Zaïri, Naït-Abdelaziz, Gloaguen, & Lefebvre, 2007; Zaïri, Nait-Abdelaziz, Gloaguen, Bouaziz, & Lefebvre, 2008), elastomeric blends (Bai & Wang, 2003) or clay/polymer nanocomposites (Faucheu et al., 2010; Gloaguen & Lefebvre, 2001).

In this study, the influence of starch plasticizing on the mechanical and plastic behaviors was investigated. Several formulations including different amounts of glycerol or other plasticizers selected purposely, mannitol and sorbitol, were prepared and studied by dynamical mechanical analysis and by video-controlled tensile tests. Additionally, the effect of aging on the deformation behavior of the thermoplastic starch blends was examined.

2. Experimental

2.1. Materials

Wheat starch was provided by Roquette (France). According to the supplier, amylose, amylopectin and protein contents were

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Table 1
Thermomechanical properties of plasticized starches.

Samples	Plasticizer content (wt%)	Young's modulus, E (MPa)	Tensile stress at break, σ (MPa)	Tensile strain at break, ε (%)	$T\alpha$ (°C)	$T\beta$ (°C)
WG70/30	30% glycerol	13 ± 3	2.7 ± 0.3	52.6 ± 3.8	15.1	−52.6
WG75/25	25% glycerol	8 ± 1	2.6 ± 0.2	60.5 ± 3.5	28.7	−44.6
WG80/20	20% glycerol	10 ± 2	4.1 ± 0.4	81.7 ± 1.9	48.2	−42.2
WG85/15	15% glycerol	1375 ± 162	12.6 ± 1.5	1.1 ± 0.3	64.9	−42.8
WS75/25	25% sorbitol	508 ± 46	14.6 ± 2.5	57.8 ± 7.9	68.1	−7.9
WM75/25	25% mannitol	3711 ± 662	16.4 ± 5.2	0.6 ± 0.2	>80	−0.2
WGS75/25	12.5% glycerol + 12.5% sorbitol	27 ± 3	6.5 ± 0.6	75.1 ± 4.5	34.7	−30.5

respectively 25, 75 and 0.2%. Glycerol (>98% purity – Fluka Analytical), sorbitol (>98% purity – Carl Roth) and mannitol (>98% purity – Carl Roth) were used as plasticizers.

2.2. Preparation of plasticized pellets

Starch was plasticized by the different polyols added in amounts ranging from 15 to 30 wt% of the total blend for glycerol and with a reference content of 25 wt% for sorbitol and mannitol (Table 1). The native starch was weighted and introduced into an internal mixer. The plasticizer or the mixture of plasticizers was added (together with a quantity of water in some formulations as a processing-aid). The blend was mixed for 15 min and then left inside the mixer for 24 h in order to allow for the complete diffusion of the plasticizer into the starch granules.

The powder mixture was extruded with a co-rotating twin-screw extruder (BC 45, Clextral, France) at barrel temperature ranging from 100 to 130 °C and at screw speed of 50 rpm and finally pelletized.

2.3. Preparation of samples

Tensile and DMA samples were elaborated using starch pellets previously obtained and extruded in a single-screw extruder (Rheoscam 20 11, Scamex, France) at 70 rpm and equipped with a plate die (3 mm × 1 mm). The temperature profile was 105–110–110–115 °C from feeder to die. Samples normalized ISO 8256:2004 type 3 were obtained by die-cutting extruded strips and stored two weeks at 23 °C and 50% RH before characterization during two weeks before characterization tests. Tensile and DMA analyses were also performed at 50% RH and 23 °C.

2.4. Dynamic mechanical analyses

The viscoelasticity measurements were conducted with a DMA (DMA 2980, TA Instrument, USA) working in the dual cantilever mode at 1 Hz with a preload of 0.01 N and with oscillation amplitude of 20 μm. The temperature range was −60 to 100 °C with a heating rate of 3 °C/min. DMA specimens were cut from tensile samples in rectangular shape with dimensions of 35 mm in length, 8 mm in width and 1.2 mm in thickness. The samples were coated with a silicone-based hydrophobic grease in order to limit dehydration during experiments conducted above room temperature (Lourdin, Bizot, & Colonna, 1997). It was checked that the thin coating of grease had no significant effect on measured thermomechanical properties.

2.5. Video-controlled tensile testing

The mechanical behavior of plasticized starches was experimentally investigated by tensile tests. The stress–strain-volumetric measurements were performed with a VideoTraction® system (Apollor, Vandoeuvre-lès-Nancy, France) mounted on a testing machine (model 5500R, Instron, USA) equipped with a 1 kN capacity load cell. Four dot markers were printed with black ink on the tensile specimens and a digital video camera recorded their relative displacements on tensile and transversal axis during the tensile test. Mechanical data analysis (stress, strain, volume strain) was performed in real time, while the axial strain was dynamically regulated at a constant nominal strain rate (G'Sell et al., 2002).

From the mechanical video-controlled recordings, the sample deformation can be decomposed into three deformation modes: inelastic volumetric, elastic volumetric and plastic deviatoric.

The volumetric strain, ε_v, was the sum of the axial strain, ε_2, and the transverse strains, ε_1 and ε_3, measured in the region where the deformation was localized:

$$\varepsilon_v = \ln\left(\frac{V}{V_0}\right) = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 \quad (1)$$

The technique is based on the assumption of transverse strains isotropy. Thus, ε_1 and ε_3 are assumed equal. In addition to true strains, the method allowed the simultaneous recording of the applied force F which can be converted into true axial stress σ:

$$\sigma = \frac{F}{A} = \frac{F}{A_0 \cdot \exp(\varepsilon_1)^2} \quad (2)$$

where A and A_0 are the instantaneous and initial sections, respectively. The inelastic volumetric strain, ε_{inel}, includes all phenomena related to damage and molecular chain orientation and is defined as:

$$\varepsilon_{inel} = \varepsilon_v - \varepsilon_{el} \quad (3)$$

where ε_{el} is the elastic part of the volumetric strain given by:

$$\varepsilon_{el} = \frac{(1 - 2 \cdot \nu) \cdot \sigma}{E} \quad (4)$$

with ν and E, the elastic Poisson's ratio and the Young's modulus, respectively.

The plastic deviatoric strain, ε_{dev}, can be deduced from previous strains:

$$\varepsilon_{dev} = \varepsilon_2 - (\varepsilon_{el} + \varepsilon_{inel}) \quad (5)$$

3. Results and discussion

3.1. Dynamic mechanical analyses

Mechanical properties of starch materials have been widely studied but mainly through classical strain-stress curves (Follain et al., 2006; Jansson & Thuvander, 2004). We propose a more precise study of the different deformation mechanisms and of their role in plasticized starch properties. The objective is to investigate the well-known effect of different factors on the mechanical macroscopic behavior as the type of plasticizer, the amount of plasticizer and the material aging from the viewpoint of deformation mechanisms. For each formulation the two transitions, characterized by a maximum of tan δ, were found at low and high temperatures and are associated respectively to β and α relaxations. The observation of two glass transitions in plasticized starch materials was

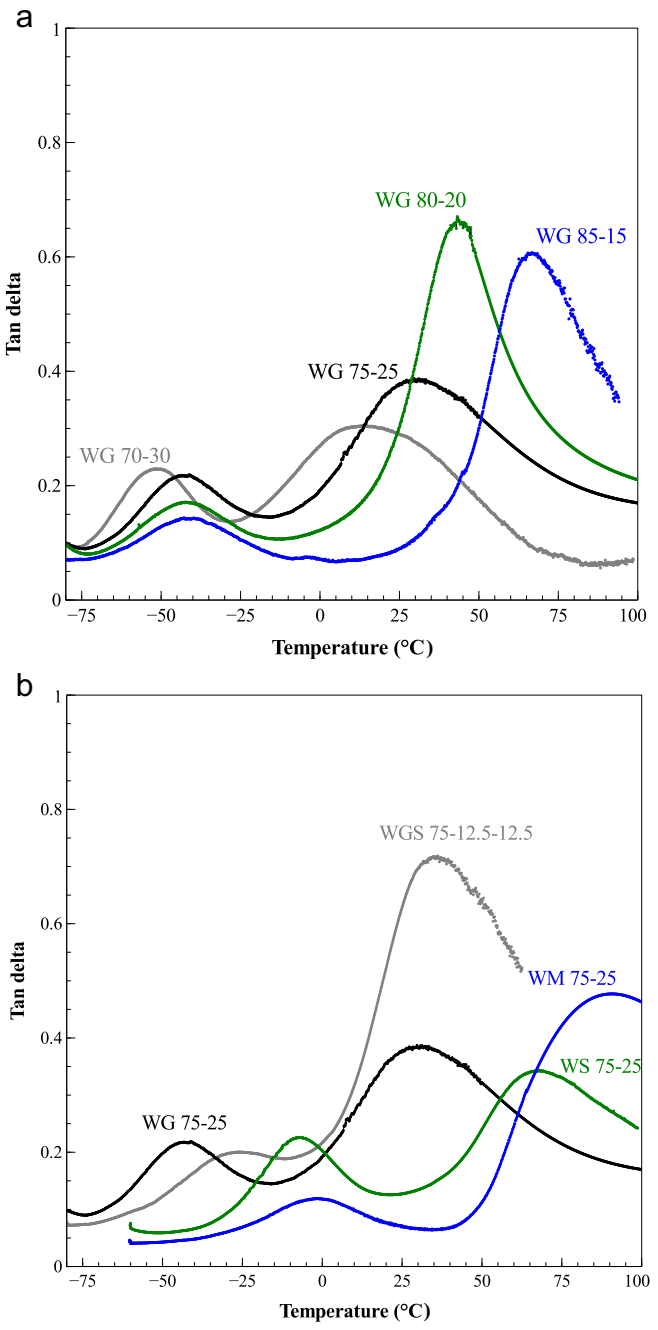

Fig. 1. Tan δ curves obtained by DMA measurements (a) with different amount of glycerol and (b) with different plasticizers.

previously described in literature (Forssell, Hulleman, Myllärinen, Moates, & Parker, 1999; Gaudin et al., 2000) and was explained by the separation of the mixture into plasticizer-rich and starch-rich phases. The β transition (<0 °C) is attributed to the plasticizer-rich phase and the α transition (>0 °C) is attributed to starch-rich phase.

Different systems have been studied and are presented through DMA results in Table 1 and in Fig. 1. Through the diversity of α transition and β transition temperature, the objective is to obtain a general view of plasticization and antiplasticization effects on deformation mechanisms. The plasticization can be described as a softening of the material due to the addition of small molecules (the plasticizers). This phenomenon is characterized by a decrease of the glass-transition temperature *Tg*, an improvement of the flexibility and an increase of material ductility. The antiplasticization phenomenon induces opposite effects on the material, except for the variation on the *Tg* and could induce a negative volume change (Gaudin et al., 2000; Lourdin, Bizot, et al., 1997; Lourdin, Colonna, & Ring, 2003).

For starch plasticized with glycerol it was found that glass transition decreases when the glycerol content increases. Lourdin, Coignard, Bizot, and Colonna (1997) have shown that it is possible to apply the Couchman's relation to follow this variation of starch as function of glycerol content. This relation seems pseudo linear in the studied temperature domain.

Differents polyols have been used as plasticizers, not only for their different efficiency (α transition position), but mainly because they have different β relaxation temperature and so differents antiplasticization behavior.

WG75/25 exhibits the lowest β transition temperature followed by WGS75/25, WS75/25 and WM75/25. The same order is observed for the glass transition temperature.

Samples plasticized with a blend of sorbitol and glycerol (WGS75/25) present a β transition around −30.5 °C which is found to be between samples plasticized exclusively with glycerol (WG75/25 $T\beta = -58.5$ °C) and sorbitol (WS75/25 $T\beta = -7.9$ °C). On the other hand, α transition of WG75/25 and WGS75/25 are relatively close (28.3 °C and 34.7 °C) while the one for WS75/25 is clearly higher (68.02 °C). Sorbitol probably disturbs local chain mobility ($T\beta$ value) of the glycerol–sorbitol blend at low temperatures while glycerol seems to control the main relaxation.

Similar relaxations temperatures have been found in the literature for glycerol and sorbitol at different contents (Gaudin et al., 2000; Lourdin, Coignard, et al., 1997) (for 25% sorbitol, $T\alpha = 53$ °C and $T\beta = -10$ °C).

Samples formulated with mannitol present the highest transitions temperatures values ($T\beta = -0.22$ °C and $T\alpha > 80$ °C). Though sorbitol and mannitol are isomers, it was found that they exhibit distinct behaviors, mannitol tending to crystallize on the sample surface after few days (Cao, Yang, & Fu, 2009), preventing the plasticization behavior which can explain such high transition temperatures.

DMA data show it was possible to obtain materials with variables glass transition temperatures from 15 °C to >80 °C, β transition temperatures from −60 °C to −0.2 °C and combinations of materials with equivalents $T\alpha$ but different $T\beta$. This set of materials will enable us to study different variety of deformation mechanisms.

3.2. Example of mechanical properties and associated deformation mechanisms

The tensile properties of WG75/25 are given in Table 1 and the corresponding true stress/true strain curve is presented in Fig. 2a. This curve shows a viscoelastic and ductile behavior of this plasticized starch.

Fig. 2b–d shows also the different contributions of the volume variation of WG75/25 sample during a tensile test: (b) the elastic volumetric strain, the purely elastic part due to the Poisson effect, (c) the inelastic volumetric strain corresponding to the degree of debonding damage, the microvoid formation, the cavitation and/or the crazing and (d) the plastic deviatoric strain, the shear banding (Addiego et al., 2006; Bouaziz et al., 2007). The contribution to the volume variation is essentially associated to inelastic volumetric strain part. Similar behavior (not presented here) was observed for WS75/25. The ductility of WM75/25 is much lower than ones of other formulations; the cavitation contribution is very higher in the case of mannitol-based materials.

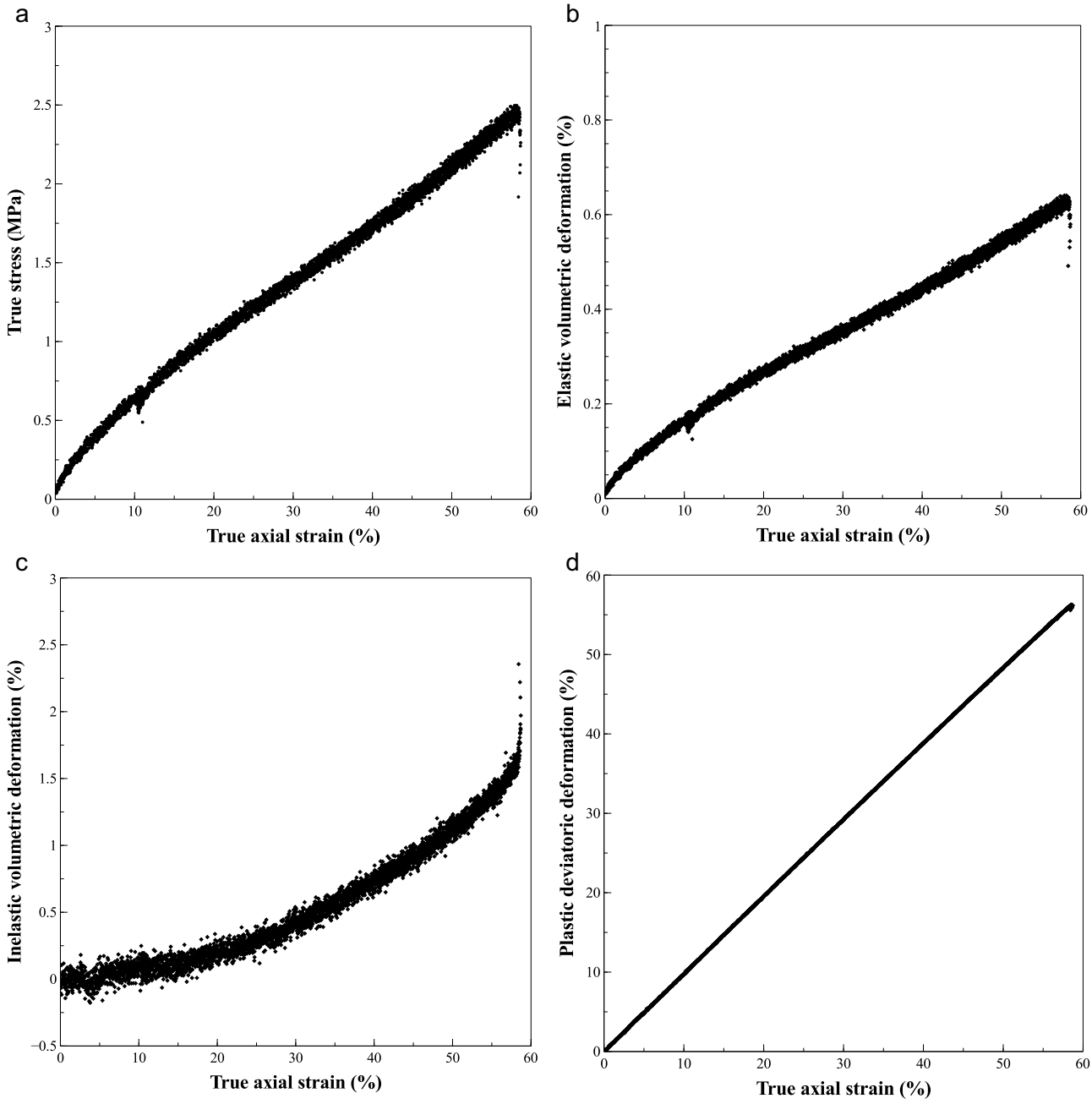

Fig. 2. (a) True stress/strain curves of WG75/25 and the different contributions, (b) elastic volumetric, (c) inelastic volumetric and (d) plastic deviatoric strains of WG75/25 under tensile deformation at true strain rate of 2×10^{-3} s^{-1}.

3.3. Influence of plasticizer amount on plastic deformation behavior

3.3.1. Deformation contributions as a function of true strain

Typical true stress–true strain and volume strain depending on true strain curves at different glycerol content are presented in Fig. 3. For each sample, one curve was chosen to be representative of the average behavior for the different materials. The tensile properties obtained from the average of all the tests are gathered in Table 1.

WG85/15 is typically a glassy material with high stress, high young modulus and low strain at break. From WG85/15 to WG80/20 a classical plasticization effect occurs: stress at break decreases while strain at break increases. From WG80/20 to WG75/25 and WG70/30, both strain and stress at break decrease. This behavior is probably due to phase separation between starch and plasticizer (Godbillot et al., 2006; Lourdin et al., 1998; Yu, Wang, Wu, & Zhu, 2008).

In all cases, volume strain (Fig. 3b) is low even at high strain levels. It means that the plastic deformation mainly occurs through plastic deviatoric strain namely shear banding. During the early stage of deformation (elastic stage), whatever the plasticizer content, volume strain corresponds to the reversible dilatation under the effect of the hydrostatic stress (Poisson's effect).

For highly plasticized materials (WG75/25 and WG70/30) the volumetric strain increase almost linearly with true axial strain but remains at a relatively low rate (in both cases around 1% at 50% of true axial strain). It means that for these highly plasticized materials, limited volumetric strain occurs during plastic deformation. This behavior could be explained by phase separation which

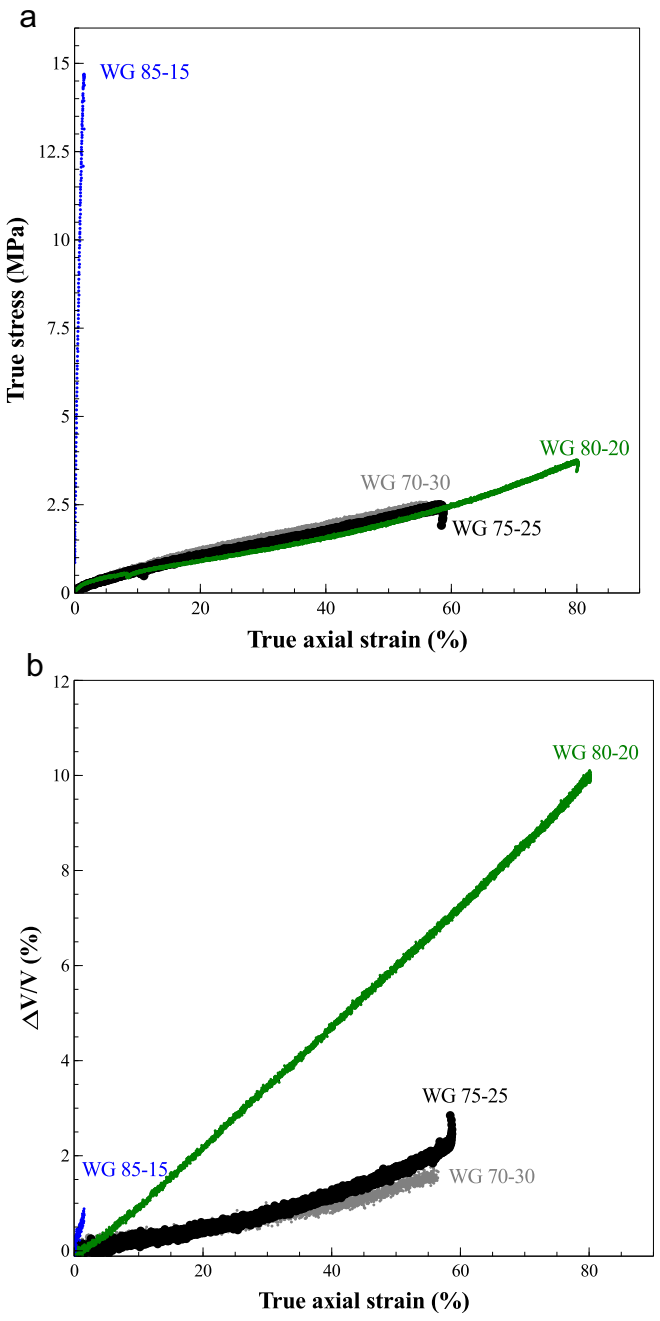

Fig. 3. (a) Typical true stress–strain curves and (b) variations of volume strain at different glycerol content.

occurs due to the excess of plasticizer. Free glycerol is present and intermolecular interactions are so low that starch macromolecules just slip from each others, easing plastic deformation through shear banding. Ponçot, Addiego, and Dahoun (2013) have found similar results with a weak volumetric deformation when the polymer-chain mobility is increased in the case of viscoelastic state of semi-crystalline polymers (polypropylene/ethylene-propylene rubber and high-density polyethylene) and an amorphous polymer (polyethylene terephtalate)

For a lower content of glycerol, in the case of WG80/20, the volume strain increases significantly compared to WG70/30 and WG85/25. It is noticeable that this increase, probably associated with cavitation and crazing, is concomitant with an increase of the ductility (strain at break). It tends to show that in the case of plasticized starch materials the presence of volumetric strain tends to favor more ductile plastic deformation. For WG85/15, no plastic deformation is observed and materials breakage is observed before yield stress. Moreover, high volumetric deformations level is reached even at low true axial strain leading to highly brittle behavior.

In term of volumetric strain, Bouaziz et al. (2007) and Zaïri et al. (2008) have shown for an unsaturated polyester reinforced with glass fibers an increase of the contribution in volumetric deformation (5% for 13% of fibers to 10% for 34% of fibers) while cavitational deformation appears later for higher fiber content. A similar phenomenon is observed with polyamide-6 and nanocomposite based polyamide-6 (Gloaguen & Lefebvre, 2001). These results are attributed to weak interfacial bond strength and microvoid formation. In opposition to this filler effect, glycerol seems to contribute to the reduction of void formation when the material is solicited by improving long distance chain movements.

3.3.2. Deformation contributions at break

Another approach to analyze deformation mechanisms consists in comparing the level of volume strain relatively to the total true axial strain at 50%. At this strain level, the materials have undergone significant plastic deformation. Therefore, the volume strain is representative of volumetric damages occurring during plastic deformation. As WG85/15 was not considered for this comparison as no plastic deformation is observed for this material.

The contribution of volume strain (volumic dilatation of the material during deformation) to the true axial strain is a third of volume strain value. As the glycerol content increases, the contribution of volume strain to axial deformation (at 50%) decreases from 5.9% for WG80/20 to 1.6% and 1.3% for WG75/25 and WG70/30 respectively (Fig. 3b). Hassouna et al. (2011) have described the same phenomenon (the inhibition of volume deformation in function of the plasticizer amount) on a polylactid (PLA) plasticized by poly(ethylene glycol) (PEG). As shown by DMA and mechanical results, WG80/20 is in glassy state while WG75/25 and WG70/30 are enough plasticized to be in the rubbery state at ambient temperature. The decrease volume strain as a function of glycerol content could then be explained and linked to the decrease of material's glass transition temperature.

3.4. Influence of plasticizer on plastic deformation behavior

3.4.1. Deformation contributions as a function of true strain

Typical true stress–strain curves as well as the associated volume deformations for different plasticized systems are represented in Fig. 4.

Starch plasticized with mannitol (WM75/25) presents brittle behavior because mannitol exuded and recrystallized on material surface during storage (Cao et al., 2009). WG75/25, WS75/25 and WGS75/25 present a typical plasticized ductile behavior. WS75/25 shows the better compromise between strain and stress, WG75/25 the weaker and WGS75/25 presents intermediate properties. Similar results have been reported in literature (Talja, Helén, Roos, & Jouppila, 2007).

As shown previously for starch plasticized at different glycerol contents, volume strain level deformation is relatively low indicating that the main plastic deformation mechanism is plastic deviatoric strain (shear banding). First, at the early stage (elastic deformation), all the materials present the dilatation related to the Poisson's ratio. However, this dilatation is significantly higher in the case of WGS75/25. In addition, this latter material volume strain starts to rise above elastic stage and then increases linearly until the sample breaks. The volume is significantly higher compared to other plasticized materials. For WS75/25 an upturn in volume strain is observed above 10% of true axial strain and then a constant increase. Volume strain of WS75/25 is in between WGS75/25

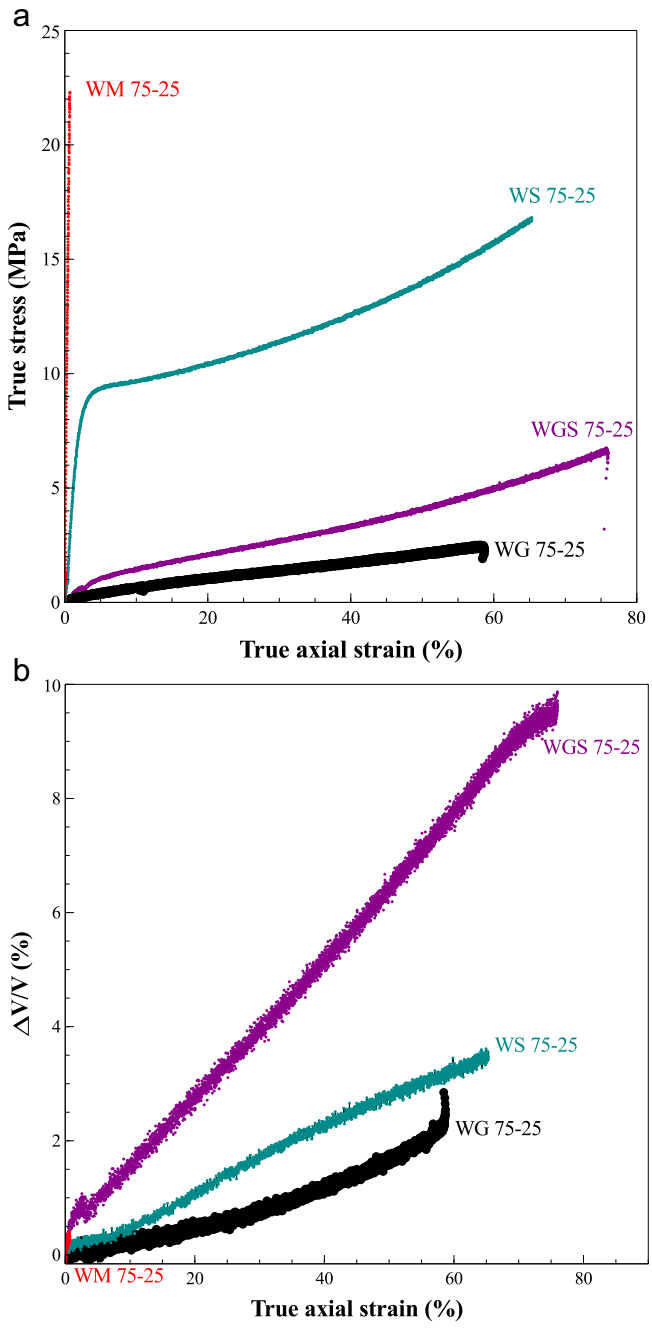

Fig. 4. (a) Typical true stress–strain curves and (b) variations of volume strain for different plasticized systems.

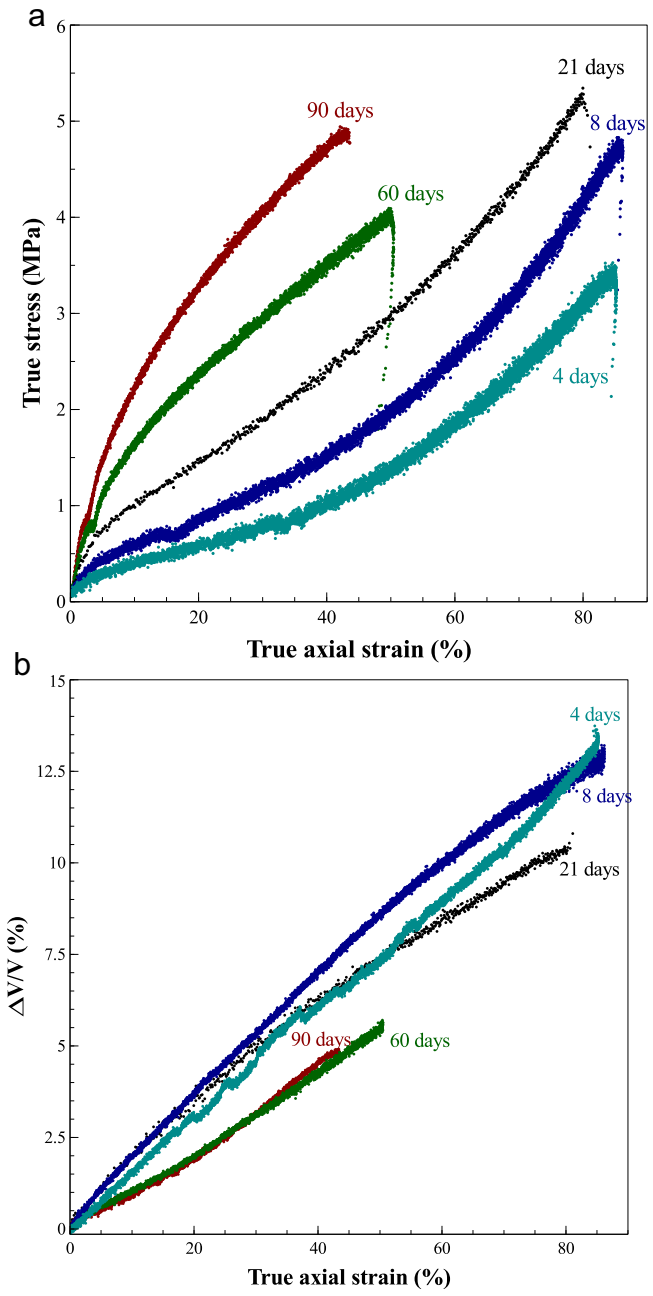

Fig. 5. Impact of aging on (a) typical true stress–strain curves and (b) variations of volume strain at 50% RH (WG80/20).

and WG7525. Actually, this latter plasticized material presents the lowest volume strain over all the plasticized materials. The behavior of WG75/25 is similar to WS75/25 with an upturn around 10% of true axial strain.

For WG75/25, the volumetric deformation is very low and the main plastic deformation mechanism is plastic deviatoric due to phase separation as explained previously. While WS75/25 presents similar deformation mechanisms to WG75/25 (with slightly higher volume strain) its tensile behavior is completely different. It could be due to the difference in α and β relaxation temperatures of the materials. Sorbitol was reported to decrease mobility of mobile parts of starch in wheat starch films at sorbitol contents below 27% (Gaudin et al., 1999) while same behavior was shown for glycerol contents below 12% (Lourdin, Bizot, et al., 1997; Lourdin, Coignard, et al., 1997). The plastic deformation behavior of these two materials should have then be different, but the observed difference can be tentatively explained (i) if both blends WS75/25 and WG75/25 include the plasticizer above its solubility limit, and (ii) if for low plasticizer contents, the deformation mechanisms are affected by antiplasticization. With respect to the second hypothesis, low volume strain of the WS75/25 sample is due to the antiplasticization effect of sorbitol, whereas it is explained by phase separation induced by glycerol excess for WG75/25.

WGS75/25 blend includes two plasticizers and presents a higher volume strain than WG75/25 and WS75/25.

3.4.2. Deformation contributions at break

For starch–glycerol systems presented previously, volume strain deformation was shown to increase when the glycerol

content decreases. This behavior can be linked to the change in $T\alpha$ of the material. The presence of higher volume strain in the plasticizer blend (WGS75/25) compared to WG75/25 and WS75/25 can then also be explained by the change in relaxation temperatures to intermediates values. The material is no more in an excess plasticizer state (WG75/25) and exhibits volume strain similar to materials plasticized with lower glycerol content as WG80/20 for example. Samples plasticized with mannitol (WM75/25) does not develop plastic deformation and presents also the highest relaxations temperatures ($T\beta$ −0.2 °C and $T\alpha$ > 80 °C). It could be compared to WG85/15 which presents also a high $T\alpha$ but a much lower $T\beta$. The difference in ductility for these two samples could be explained by (1) the recrystallization of mannitol or (2) the difference in their β relaxation temperature which is linked to local chains mobility.

3.5. Influence of aging on plastic deformation behavior

The impact of aging at 50% RH on the mechanical properties and on the deformation mechanisms of plasticized starch (WG80/20) is shown in Fig. 5.

For true stress–strain curves (Fig. 5a), the changes in elongation are related to the changes in starch structure and B-type crystallinity due to retrogradation of the material. The formed crystals act as physical crosslinks, increasing the strength of samples (Van Soest & Knooren, 1997).

We can observe that the main impact on plastic deformation is a decrease of volumetric deformation which decreases from more than 12% to ∼5% after 90 days of aging (Fig. 5b). Aging tends to promote plastic deviatoric strain to the detriment of volumetric strain leading to lower ductility of the plasticized materials. This trend is all the more pronounced as aging time is high.

4. Conclusion

In this paper, the mechanical behavior of plasticized starch was studied. The effect of the formulation was investigated with different plasticizers and different amounts of plasticizer, as well as the effect of materials aging. From different formulations, it is possible to obtain materials with different glass transition temperatures ranging from 15 °C to >80 °C, and with β transition temperatures from −60 °C to −0.2 °C. The VideoTraction® method was used to determine the deformation behavior of the plasticized starch, i.e. the true stress/true strain curves and the volume strain deformations. In all cases, the deviatoric contribution is the main part of the plastic deformation.

The plastic behavior is dependent on the plasticization state of the material. With respect to the role of sorbitol (low power of plasticization), this hexol induces an antiplasticization effect, increases the cohesion in the material and reduces the volume strain. In the case of glycerol (more efficient plasticizer), the mobility of polymer chains is increased. However, an excess of glycerol induces a phase separation and limits the volume deformation. In the case of plasticized starch based on a blend between glycerol and sorbitol, the glycerol seems to control the main relaxation and sorbitol disturbs local chain mobility. Mannitol tends to exude and crystallize onto the surface of material after few days and this starch based material is brittle and breaks before plastic deformation. The aging of material impacts the deformation behavior because the retrogradation of starch induces physical crosslinks in the material and decreases the volume strain.

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