Deformation mechanisms of plasticized starch materials

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ARTICLE INFO

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.

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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:

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

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:

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

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:

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

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

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

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:

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

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