



Mechanical and ultimate properties of injection molded cellulose acetate/plasticizer materials

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ABSTRACT

The mechanical properties of injection molded plasticized cellulose acetate polymers processed with two different plasticizers (Triacetine and Diethyl phthalate) and various weight fractions comprised between 15 and 30 wt % have been investigated. Plasticized cellulose acetate exhibit a brittle-to-ductile transition from a low impact strength to a high impact strength of order 40 kJ/m². Obtaining a high impact resistance at room temperature requires plasticizer content larger than 25 wt.%. An important strain hardening is obtained for samples with both plasticizers during tensile experiment. At 15 wt.% plasticizer content, the measured strain hardening modulus is around 148 MPa at 60 °C. Different parameters influencing the strain hardening behavior have been identified: the tensile direction as compared to that of the injection flow, the temperature and the plasticizer, consistent with studies on pre-strained samples of synthetic amorphous polymers.

1. Introduction

Due to its biodegradability and renewability (Klemm, Heublein, Fink, & Bohn, 2005), a great interest has been dedicated to investigating cellulose acetate polymers in order to expand its potential applications.

The need for renewable materials has led to a renewed interest in studying processing and properties of cellulose derivatives over the past few years. It has growing applications in textile (Law, 2004), food pharmaceutical and material engineering industries (Carollo & Grospietro, 2004). Melt processing of cellulose based thermoplastic polymers is a real challenge. One problem is the existence of a narrow window between the melting point and the degradation temperatures for cellulose acetate with a substitution degree (DS) around 2.45 (Zugenmaier, 2004). As a consequence, its processing can only be considered with a sufficient amount of external plasticizer. Extensive research has been dedicated for identifying efficient plasticizers (Fordyce & Meyer, 1940) but its effect on processing and properties have not been studied in detail (Mohanty, Wibowo, Misra, & Drzal, 2003). The corresponding polymer/plasticizer blends are amorphous (Zugenmaier, 2004) and their mechanical properties are mainly governed by the presence of a high volume fraction of strong hydrogen bonds (Zugenmaier, 2004). Many studies have been carried out for characterizing the miscibility, the plasticization and the mechanical

properties of commercial cellulose acetate with a DS of 2.45 (CDA) and its plasticized samples prepared via solvent casting method (Bao, Long, & Vergelati, 2015). Differential Scanning Calorimetry (DSC) (Scandola & Ceccorulli, 1985a), Differential Mechanical Thermal Analysis (DMTA) (Scandola & Ceccorulli, 1985b) and Broad Band Dielectric Spectroscopy (BDS) (Bao, 2015; Sousa et al., 2010) have been used to study molecular motions in a wide frequency range regarding the α - and the β -relaxations, miscibility behavior and plasticizing effect on these plasticized CDA samples.

Few studies have been published regarding the mechanical properties of bulk cellulose acetate (prepared via injection molding) (Ishikawa & Tadano, 1987; Mohanty et al., 2003; van De Ven & Kadla, 2013; Warth, Mülhaupt, & Schätzle, 1996). Among these studies, the majority is focused on mechanical properties of cellulose acetate fibers (Zugenmaier, 2004). (Mohanty et al., 2003) have studied the influence of three type of processing on the mechanical properties of plasticized CDA. The authors studied the impact strength (obtained by the so-called IZOD measurement, standard method of determining the impact resistance of materials), the tensile strength and the elongation at break. They reported that materials processed by extrusion followed by injection molding exhibited better properties as compared to those processed by extrusion followed by compression molding. Mechanical and optical properties of plasticized cellulose acetate have been studied by (Ishikawa & Tadano, 1987) on samples obtained via solvent casting.

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The stress-strain relation of cellulose acetate was studied by uniaxial tension test under various strain rates and temperature. The mechanical properties described in this work (elongation at break around 15% and yield stress around 40 MPa, Young modulus around 2000 MPa) are comparable to those of PS, styrene acrylonitrile copolymers (SAN) or poly(methyl methacrylate) (PMMA). Mechanical properties of plasticized cellulose acetate have proven to be particularly interesting (Carollo & Grospietro, 2004; Zugenmaier, 2004). Cellulose acetate based materials usually display a high Young modulus (Zugenmaier, 2004). But its small deformation at break amplitude limits its potential for new applications. However, its current properties makes it a more promising candidate than other bio-based polymers such as starched derivatives (Sahari, Sapuana, Zainudinb, & Malequed, 2013; Stepto, 2009), provided one succeeds in improving its impact properties.

The objective of this paper is to study the effect of plasticizing molecules on mechanical properties. Two different plasticizers are considered, triacetin (TA) and diethyl phthalate (DEP). All plasticizer/CDA systems are prepared by extrusion and various injection molding conditions with various amounts of plasticizers comprised between 15 wt% and 30 wt%. The impact strength will be described in Section 3.2 and tensile behavior in Section 3.3, as functions of plasticizer contents, process conditions over a broad strain rates and temperature ranges.

2. Experimental section


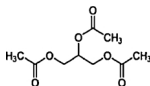
2.1. Material

Eight samples are used in this study: two plasticizers (TA and DEP) and four plasticizer contents for each plasticizer. All compositions are listed in Table 1. TA is an eco-friendly plasticizer and DEP is the historic plasticizer of cellulose acetate which constitutes a reference for this work as it is usually the case in the literature. Cellulose acetate sample with an average DS of 2.45 (CDA) is supplied by Acetow GmbH (Freiburg, Germany). DEP and TA are obtained from Sigma Aldrich (Saint Quentin Fallavier, France). CDA with a DS of 2.45 is chosen because according to Kamide and Saito (Kamide & Saito, 1984), the limited range of DS ~ 2.5 is the only cellulose acetate whose melting temperature ($T_m = 505^\circ\text{K}$) is lower than the degradation temperature ($T_d = 509^\circ\text{K}$). The corresponding polymers can be melt processed and injected with external additives.

2.2. Extrusion and injection molding

Diethyl phthalate plasticized cellulose diacetate (DEP-pCDA) or triacetin plasticized cellulose diacetate (TA-pCDA) samples in the desired weight amount (between 15% and 30%) are prepared by extrusion. A specific amount of external plasticizer and CDA powder (dried in a vacuum oven at 70°C during 24 h) is fed into a twin-screw Cleextral extruder (L/D ratio 48). The temperature profile is kept between 170°C and 200°C (Warth et al., 1996). At lower plasticizer contents a higher temperature in the extruder is required. Screw speed is varied between 400 rpm and 500 rpm. At lower plasticizer content a faster screw speed is needed to have a stable process. Debit is kept constant at 20 kg/h for all compositions. Residence time is approximately 5 min. Because of the thermosensitivity of cellulose acetate the profile of the screw is adapted

Table 1
Structure of plasticizer and their contents (wt%) in CDA systems.

DEP	TA	Content (wt%)
		15
		20
		25
		30

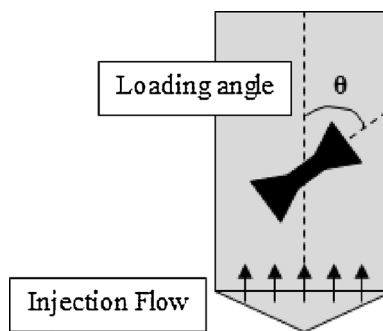


Fig. 1. Schematic top view of the injection molded plate. The sample is cut with an angle θ from the injection direction.

to limit self-heating.

After extrusion, we have defined three injection modes. First, the process A: formulations are injection-molded into tensile and impact strength specimens with a Billion 100 T injection press. Mold temperature is kept at 30°C . Tensile and impact strength specimens dimensions are $150 \times 10 \times 4 \text{ mm}^3$ and $80 \times 10 \times 4 \text{ mm}^3$ respectively (ISO-527 and ISO-157 norms).

Second, the process B: plates with dimensions of $350 \times 100 \times 4 \text{ mm}^3$ are injected with a Billion 750 T BI-MAT injection press. Mold temperature is kept at 80°C . For the plate specimens, the mold included a v-shaped runner with a ramp. The flow in front of the polymer melt is uniform across the width of the plate, as shown in Fig. 1. Based on observations on glass fibers reinforced semi-crystalline polymers, we assume that the injection molding process into plates leads to a homogeneous orientation of polymer macromolecules in the thickness of the plates (Rolland, Saintier, Wilson, Merzeau, & Robert, 2017). Tensile specimens (ISO-527 norms) are directly cut into these plates.

Third, the process C: tensile bars with the following dimensions $92 \times 14 \times 4 \text{ mm}^3$ and with a radius of curvature larger than ISO-527 are directly manufactured by cutting them from the plate at different angles θ with respect to the main flow direction. This angle θ ranges from 0° to 90° . This is illustrated in Fig. 1, where a tensile specimen is schematized at a loading angle $\theta = 45^\circ$. The specimen's geometry is designed specifically in order to study strain hardening behavior of pCDA.

2.3. Characterization methods

2.3.1. Modulated differential scanning calorimetry (MDSC) and dynamic mechanical thermal analysis (DMTA)

The molecular mobility of plasticized samples is characterized by modulated differential scanning calorimetry MDSC and DMTA. MDSC measurements are performed by using a Q2000 differential scanning calorimeter (TA instruments, United States) equipped with a liquid N_2 cooling device (LNCS). Indium is used for temperature and heat flow calibration of our MDSC apparatus. Sapphire is used to calibrate the MDSC reversing heat capacity signal. For each measurement, 5–10 mg of polymer are sealed into a Tzero aluminum pan and placed in the autosample. Samples are preconditioned at 30°C for 10 min for equilibration. Thermograms are recorded during heating at a scanning rate of $5^\circ\text{C}/\text{min}$. Modulation is performed every 40 s at $\pm 2^\circ\text{C}$. Glass transition temperatures are determined from the second scan, in order to discard the influence of thermal history, at the inflexion point of the heat capacity jump. A rheometric Scientific analyzer RSAGII (TA instrument) is used to perform dynamic mechanical thermal analysis DMTA measurements. Impact specimens are used to characterize the mechanical relaxations, using the three-point bending method. A strain limit is fixed at 0.03%. Curves are recorded at fixed frequencies 0.1 Hz, 1 Hz, 10 Hz and 50 Hz during heating from -120°C at a scanning rate of $2^\circ\text{C}/\text{min}$ to 200°C . Relaxation temperatures are determined from the peak of $\tan \delta$ plot.

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