Polymer Degradation and Stability 98 (2013) 1556–1562

Contents lists available at SciVerse ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Polymer Degradation and Stability

Enhancement of cellulose acetate degradation under accelerated weathering by plasticization with eco-friendly plasticizers

Robert Quintana [a,b,c], Olivier Persenaire [a,b], Yahia Lemmouchi [d], John Sampson [d], Stuart Martin [d], Leïla Bonnaud [a,b], Philippe Dubois [a,b,*]

[a] Materia Nova asbl, Parc Initialis, Avenue N. Copernic 1, 7000 Mons, Belgium
[b] University of Mons UMONS, Place du Parc 20, 7000 Mons, Belgium
[c] Institute of Materials Research and Engineering (IMRE), A*STAR, 3 Research Link, Singapore 117602, Singapore
[d] Group R&D Centre, British American Tobacco, Regents Park Road, Millbrook, Southampton SO15 8TL, UK

ARTICLE INFO

Article history:
Received 22 September 2012
Received in revised form
24 June 2013
Accepted 27 June 2013
Available online 5 July 2013

Keywords:
Cellulose acetate
Degradation
Weathering
Plasticization
Blend

ABSTRACT

Cellulose acetate (CA) with a degree of substitution (DS) of 2.5 has been plasticized using eco-friendly plasticizers such as triacetin, tripropionin, triethyl citrate, tributyl citrate, tributyl 2-acetyl citrate and poly(ethylene glycol) of low molecular weight. Thermo-mechanical properties and hydrophilicity of the modified CA have been measured and correlated with the content and nature of the plasticizer used and compared with unplasticized CA. The increase in toughening and the change in the hydrophilicity by the plasticization were evaluated in terms of aging and weathering stability under accelerated conditions. Samples were exposed to UV-degradation with water spray periods. The treated samples were removed periodically and characterized by several analytical techniques. The results are discussed with particular emphasis toward the effects of plasticization on enhancement of the degradation rate of CA. The plasticization of CA triggered an increase of the weight loss between 50 and 90%, where low molecular weight plasticizers were shown to be more effective. A right balance between hydrophilicity and plasticization efficiency (reduction of T_g) is needed to increase the degradation rate of CA.

1. Introduction

One of the most important organic esters is cellulose acetate (CA), which is widely used for many industrial applications in the form of film and fibre [1]. CA is derived from cellulose using the acetylation process and its main properties are its hardness, good resistance to impact, high shine, transparency, pleasing texture, lack of static electricity and resistance to hydrocarbons [1,2]. Furthermore, CA has recently been reported to be potentially biodegradable [3,4] and that the biodegradation rate depends on its degree of acetyl-group substitution (DS). As DS of CA decreases, biodegradation rate increases. However, for some applications, a faster degradation rate is desirable in minimising the impact of CA products in the environment.

Plasticizers have long been known for their effectiveness in producing flexible plastics for applications ranging from the automotive industry to medical and consumer products. Plasticizers are used for biodegradable plastics as well. There are more stringent requirements on these plasticizers, though, since by definition they will be released into the environment during product use. Health and safety issues dominate the research in this field, with benign, often natural substances having nearly as great importance as the ability to lower the T_g of the polymer. Because of the prevalence and commercial applications of biodegradable polymers, recent research has focused on developing compatible plasticizers that also biodegrade [5,6]. Citrate-based plasticizers can be derived from naturally occurring citric acid. They are non-toxic and are used as plasticizers with some biodegradable polymers [7–11]. Ghiya et al. melt blended cellulose acetate (CA) with two different citric acid esters: triethyl citrate and acetyl triethyl citrate. The authors observed that both plasticizers are miscible with CA and the addition of plasticizer reduces the tensile modulus and increases the elongation of CA. The biodegradation rates are increased dramatically with an increase in plasticizer content [12]. Simple triglycerides as triacetin can be used as a food additive and is already applied to cigarette filter as a plasticizer [13]. The high boiling point of triacetin compared to citrate-based plasticizers (Table 1) reduces the amount of plasticizer loss occurring during melt processing, especially with the lower MW citrates [10].

---

[*] Corresponding author. University of Mons UMONS, Place du Parc 20, 7000 Mons, Belgium. Fax: +32 65 373484.
E-mail address: philippe.dubois@umons.ac.be (P. Dubois).

0141-3910/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymdegradstab.2013.06.032

Table 1
Boiling points and densities of triacetin and citrate-based plasticizers.

Plasticizer	Boiling point (°C)	ρ (g/cm^3)
Triacetin	259	1.15
Tributyl citrate	169	1.10
Triethyl citrate	126	1.14
Acetyl tributyl citrate	173	1.05
Acetyl triethyl citrate	131	1.14

Polyols are another class of compounds which have been studied as plasticizers for biodegradable polymers. Glycerol, which is often used with biodegradable polymers, was found to reduce thermal degradation of thermoplastic starch (TPS) reinforced with cellulosic fibres [14]. However, the lower miscibility of glycerol in acetone reduces its application by solvent blending with CA. Poly(ethylene glycol) (PEG) is a flexible and water-soluble polymer and also soluble in acetone. Rosa et al. reported that blending CA with PEG(400) or PEG(1500) decrease the T_g of CA and enhances the tensile strength of CA [15]. The authors pointed out the effect of the interactions between the free hydroxyl groups of PEG and the chains of CA as an explanation of the enhanced the resistance of CA [15].

The present study focused on the use of eco-friendly plasticizers as modifiers for CA2.5 (DS = 2.5) and their effects on thermo-mechanical properties and weathering stability of the related polymer materials. To our knowledge, the relationship between CA plasticization and weathering stability has never been reported. The aim of the study was to increase the degradation rate of CA by blending CA with water soluble plasticizers.

2. Experimental

2.1. Materials

Cellulose Acetate (flakes, $M_n = 65.400$ and polydispersity index of 3.4) (CA) with a degree of substitution of 2.5 was kindly supplied by British American Tobacco. Triacetin (TA) was purchased from Acros. Tripropionin (TP), triethyl citrate (TeC), tributyl citrate (TbC) and tributyl 2-acetyl citrate (Tb2C) were purchased from Merck and Poly(ethylene glycol) 200 (PEG) from Fluka. These chemicals and solvents used in this study were all guaranteed reagent grade and used without further purification.

2.2. Procedures

2.2.1. Film preparation by solvent casting and melt processing

Films of blends of CA and plasticizers were prepared by both solvent casting and melt processing methods. The films were cast by being drawn on Petri dishes 10% solutions (w/w) of the materials in acetone. The thickness of the films was approximately 0.5 mm after the removal of the solvent. Melt blending of CA (dried overnight at 105 °C in a ventilated oven) with plasticizers was performed in a Brabender internal mixer (model 50 EHT, 80 cm^3 free volume) equipped with cam blades at 235 °C and 60 rpm during a total time of 10 min. 500-μm films were prepared, immediately after blend preparation, by hot-pressing moulding at 235 °C using an Agila PE20 hydraulic press (low pressure for 120 s without degassing cycle, followed by a high-pressure cycle at 150 bars for 180 s and cooling by tap water at 50 bars for 120 s).

2.2.2. Aging

The plasticized CA films were boxed and aged at room conditions for 3 months. The films were then characterized with MDSC in order to investigate the stability of the blends.

2.2.3. Accelerated weathering

Accelerated weathering testing was performed in a Q-Sun Xenon arc test chamber with a wavelength range of 295–800 nm and the Daylight-Q filter. The Daylight-Q filter produces a spectral power distribution equivalent to noon summer sunlight. The irradiance setting used was 0.65 W/m^2 calibrated at 340 nm. The irradiance is relatively homogeneous in the chamber (only around a 10% drop from the maximum exposure in the centre of the shelf to the periphery). Square (3 × 3 cm) specimens were exposed to 0.65 W/m^2 at a chamber temperature of 50 °C and a relative humidity of 50% up to 475 h. The samples were water sprayed during 30 min of each 5 h cycle. Samples were placed perpendicular to the irradiation into sample cups of 92 mm of diameter with three films placed in each cup. After each time period, a film was removed for further characterization.

2.3. Measurements

The number average molecular weights and molecular weight distributions of the polymers were determined in THF at 23 °C using a Agilent size exclusion chromatograph equipped with a Knauer 2320 refractometer index detector and two PLGel columns (MIXED-D and 103A). Samples were dissolved in THF (5 mg/1 ml), 20 μL of the solutions were injected into the columns using a flow rate of 1 mL/min. Monodisperse polystyrene standards (Polymer Laboratories Ltd.) were used for the primary calibration.

Differential scanning calorimetry (DSC) measurements were performed by using a DSC 2920 from TA Instruments calibrated with indium under nitrogen flow (50 mL/min). The following procedure was used: first heating at 20 °C/min from room temperature to 150 °C, keeping at this temperature for 60 s to eliminate the dehydration, which occurs around 120 °C [16,17]. Then the temperature was reduced to 30 °C at 10 °C/min and finally a heating scan at 10 °C/min to 270 °C.

Modulated DSC spectra were obtained using an MDSC 2920CE from TA Instruments calibrated with indium under nitrogen flow (50 mL/min). The samples was heated at 20 °C/min from room temperature to 150 °C and held there for 60 s. Then the temperature was reduced to 30 °C at 10 °C/min and finally the sample was heated to 270 °C at 5 °C/min while applying a temperature oscillation of 1 °C/min.

Thermogravimetric analyses (TGA) were performed by using a TGA Q500 (TA instruments) with a heating rate of 20 °C/min in air, from room temperature to 800 °C (platinum pans, 60 cm^3/min air flow rate). High resolution TGA analyses were performed on a Hi-Res TGA 2950 from TA Instruments, using nitrogen as purge gas and a resolution parameter of 5, which means that a continuously variable heating rate is applied in response to changes in the sample decomposition rate. This resolution parameter can be tuned within an eight-step scale to maximize weight loss resolution.

Tensile testing measurements were performed by using a Lloyd LR 10K tensile bench in accordance with ASTM D 882 “Standard Test Method for Tensile Properties of Thin Plastic Sheeting”, standard at room temperature using a crosshead speed of 20 mm/min and a distance of 25.4 mm between grips. Rectangular test specimens (64 × 10 mm) were cut from 500-μm films and were previously conditioned for at least 48 h at 20 ± 1 °C under relative humidity of 45 ± 5% and values were averaged over five measurements.

The static contact angle of water drop deposited onto film surface was measured using a drop shape analysis system (DSA 10 MK2, Krüss) at 25 °C. A drop of deionized water (20 μL) was placed onto the sample surface and the images of the water menisci on the sample surface were recorded through a digital camera. These images were analysed by DSA software to yield the contact angle values. A total of 4 measurements on different areas of the surface were averaged.