



Thermo-mechanical properties and blend behaviour of cellulose acetate/lactates and acid systems: Natural-based plasticizers

Camille Decroix, Chalamet Yvan, Guillaume Sudre, Vergelati Caroll

► To cite this version:

Camille Decroix, Chalamet Yvan, Guillaume Sudre, Vergelati Caroll. Thermo-mechanical properties and blend behaviour of cellulose acetate/lactates and acid systems: Natural-based plasticizers. Carbohydrate Polymers, 2020, 237, pp.116072. 10.1016/j.carbpol.2020.116072 . hal-02749795

HAL Id: hal-02749795

<https://univ-lyon1.hal.science/hal-02749795>

Submitted on 22 Aug 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

Thermo-mechanical properties and blend behaviour of cellulose acetate/lactates and acid systems: Natural-based plasticizers

Decroix Camille^{1,3}, Chalamet Yvan^{1,*}, Sudre Guillaume², Vergelati Caroll³

¹ Univ Lyon, UJM-Saint-Etienne, CNRS, IMP, UMR 5223, F-42023, SAINT-ETIENNE, France

² Univ Lyon, Université Claude Bernard Lyon 1, CNRS, IMP, UMR 5223, F-69100, VILLEURBANNE, France

³ Solvay in Axel'One, 87 avenue des Frères Perret CS 70061, F-69192 SAINT-FONS, France

E-mail addresses :

yvan.chalamet@univ-st-etienne.fr (Y. Chalamet) Corresponding author

camille.decroix@univ-st-etienne.fr (C. Decroix)

guillaume.sudre@univ-lyon1.fr (G. Sudre)

caroll.vergelati@solvay.com (V. Caroll)

Declarations of interest : none.

ABSTRACT

This work brings together thermo-mechanical and structural information for plasticized cellulose acetate (CA) by lactates and octanoic acid. CA are processed with plasticizer due to their high T_g and their strong H-bonding network. We prepared CA / plasticizer blends by corotative twin screw extruder and by solvent casting methods. The study of the different relaxations and of the glassy zone modulus was performed by dynamic mechanical analysis (DMA). The miscibility range of cellulose acetate blends were identified by the analysis of the tan δ . Depending on the composition of the system, one or two transitions are noted, this last result indicates the presence of a phase rich in CA and another in plasticizer. To connect this information to crystallinity and molecular organization, X-ray diffraction analyses were carried out. The disappearance of crystallinity allows the plasticization of previously inaccessible zones, causing a glassy modulus drop of more than 1000 MPa.

Keywords: Cellulose acetate, plasticization, miscibility, thermo-mechanical properties, X-ray diffraction.

1. Introduction

In recent years, the interest in biopolymers has been increasing continuously. Cellulose acetate is a biobased and biodegradable polymer manufactured from cellulose, which is one of the most abundant renewable organic resources on Earth, and excess of acetic anhydride (Wu et al., 2004). A part of the hydroxyl groups is converted to acetyl groups using esterification reactions. The most common degree of substitution (DS) is 2.5 partly due to melting properties (Kamide & Saito, 1985). To improve flexibility and processability by lowering the glass-transition, cellulose diacetate is blended with plasticizers (Lee et al., 2005; Vieira, da Silva, dos Santos, & Beppu, 2011; Wypych, 2012).

In the literature, there are many studies on thermal and mechanical properties of plasticized cellulose acetate. Samples are especially characterized by dynamic mechanical analysis and differential scanning calorimetry. (Bao, Long, & Vergelati, 2015; Kawai & Hagura, 2012; Lee et al., 2005; McBrierty, Keely, Coyle, Xu, & Vij, 1996; Scandola & Ceccorulli, 1985a; Seymour, Weinhold, & Haynes, 1979; Vidéki, Klébert, & Pukánszky, 2007).

Over the past few years, the worldwide production of plasticizers has been around 5 million tons per year. They were used in about 60 different polymers and 30 groups of products (Bialecka-Florjańczyk & Florjańczyk, 2007). Modifying polymers by the addition of plasticizers is not a recent practice in the manufacturing of plastic products. Their use began in the late 19th century. Plasticizers represent about one third of the global market of plastic additives (Rahman & Brazel, 2004).

The main plasticizers used to plasticize cellulose acetate are triacetin (food packaging & cigarette filters and other), diethyl phthalate (glasses & adhesive tape and other), triphenyl phosphate (photographic films and other) among others (Wypych, 2017). Triacetin and diethyl phthalate are among the best plasticizers of cellulose acetate due to their high boiling points (respectively 260 and 298 °C). This reduces the plasticizer weight loss during the mixing process (Quintana, Persenaire, Lemmouchi, Bonnaud, & Dubois, 2014). It should be noted though that some of the commonly used plasticizers are not eco-friendly.

There is an increasing interest for natural based plasticizers to develop new bio-based materials made from biodegradable and renewable resources. It seems to be more appropriate to use natural based plasticizers to manufacture biopolymers (Vieira et al., 2011). Lactates are esters formed from lactic acid (Pereira, Silva, & Rodrigues, 2011), and octanoic acid (OA) is a fatty acid mainly found in edible oils and milk of various species (Lizhi, Toyoda, & Ihara, 2008; Nair et al., 2005). They are natural solvents so they could be named green solvents. They have higher boiling points than other solvents which come from biomass. Ethyl lactate (ELL) and butyl lactate (BL) are particularly

attractive due to their lower vapour pressures than some traditional solvents: they have a lower VOC (volatile organic carbon) character. (Lomba, Giner, Zuriaga, Gascón, & Lafuente, 2014)

In this study, lactates and octanoic acid was used as external plasticizers of cellulose acetate to decrease the Tg and suppress the high degree of crystallinity of CA. The objectives of this work are to study the effect of these eco-friendly additives on thermo-mechanical, structural properties and morphologies of CA materials.

2. Materials & methods

2.1 Materials

CA was supplied by Acetow GmbH (Freiburg, Germany). The DS of CA was 2.45, i.e. combined acetic acid \approx 55.63 %. Ethyl lactate (ELL, \geq 98 %, food grade CAS No.: 687-47-8), butyl lactate, \geq 97 %, food grade, CAS No.: 34451-19-9) and octanoic acid (OA, \geq 98 %, food grade, CAS No.: 124-07-2) were purchased from SIGMA-ALDRICH.

^1H NMR analysis solvent acetone- d_6 and pyrrole (purity \geq 99%) were both supplied by Acros Organics.

2.2 Experimental procedure

2.2.1 Preparation of CA / plasticizer samples

In this study, two types of processing to prepare plasticized cellulose acetate were used due to the wide range of plasticizer rates under study. In fact, the extrusion process is impossible for blends containing less than 15 wt% of plasticizers due to the very low plasticization and also for blends with more than 40 wt% of plasticizers due to their very low viscosity at high temperature. So, solvent cast method was used for mixtures without or with very small amount of plasticizers and for mixtures with up to 70 wt% of plasticizers.

A corotative twin-screw extruder Clextral BC 21 was used to prepare compounds composed of 15 to 40 wt% of plasticizer, with a screw speed of 100rpm at a feeding rate of 2 kg/h. Cellulose acetate powder, dried for 72 h under vacuum at 70 °C, was inserted in zone 1 using a weight-feeder. A liquid plasticizer was injected by a volumetric pump in zone 2. The extruder was connected to a water cooling bath and a granulator.

For samples plasticized between 0 and 70 wt%, 2 g of CA / plasticizer mixtures were dissolved in 20 mL of acetone. The solutions were placed 24h under stirring and then poured into an evaporation

bell, composed of a PTFE mold closed with a perforated glass lid on the top, at room temperature during 150 h.

2.2.2 NMR Spectroscopic Measurements

¹H NMR analyses were performed by a Bruker Advance III spectrometer working at 400 MHz equipped with a 5 mm multinuclear broadband probe (BBFO+) with z-gradient coil. The solute concentration was 60 to 80 mg.mL⁻¹ in acetone d6. The analysis was performed at a 298 K temperature. To analyse and quantify internal plasticization of CA, 1/3 of the solute weight was added in pyrrol.

The amount of plasticizer was analyzed by NMR because the target concentration of a blend was not equal to the real concentration, in particular for the mixtures obtained by an extrusion process.

2.2.3 Dynamical mechanical analysis (DMA)

The dynamical mechanical analysis was carried out by means of a dynamical mechanical thermal analyser Q800 (TA instruments). A wide range of temperatures (-100 °C to +220 °C) were investigated. A constant heating rate of 2 °C.min⁻¹ and frequencies of 1 Hz were used. Transition temperatures were determined using the inflexion point of the storage modulus curve and the glassy zone modulus was determined using the minimum of tangent δ according to *C. Liu et al.* (Liu, He, Ruymbeke, Keunings, & Bailly, 2006). CA/plasticizer samples were preconditioned at 30 % of relative humidity for 60 h before thermo-mechanical analysis.

2.2.4 Small-angle X-ray scattering (SAXS) and Wide-angle X-ray scattering (WAXS)

SAXS/WAXS experiments were carried out at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France) on the BM2-D2AM beamline. The incident photon energy was set to 18 keV. Samples with a thickness between 800 and 1000 μ m were directly placed in the beam path. The SAXS and the WAXS signals were detected simultaneously using two 2D XPad solid state detectors. For SAXS acquisition, the sample-to-detector distance was set at about 1.15 m and a beam stop with a diameter of 2 mm was used. For WAXS acquisition, the sample-to-detector distance was set at 10 cm. The q-calibration ($q = 4\pi\sin(\theta)/\lambda$; 2θ : scattering angle) was achieved using a silver behenate powder standard for SAXS and a chromium(III) oxide (Cr₂O₃) powder standard for WAXS. The scattering contribution of air was subtracted from the scattering intensity of the samples. The image data treatments took into account the flat field response. The intensity was further normalized by the incident flux, and the sample thickness and I-calibration were achieved with a glassy carbon standard. The scattering profiles of the intensity I as a function of the scattering vector q were obtained by azimuthally averaging the corrected images.

2.2.5 Scanning electron microscope (SEM)

The morphology of the samples was observed by a scanning electron microscope (Hitachi S 3000 N) with a tungsten filament and high vacuum operated at 10 kV. The surface of samples was prepared with a cryo-ultramicrotome RMC MTXL. All the samples were gold-palladium-coated by sputtering to produce electrical conductivity.

3. Results and discussion

3.1 Thermal properties of systems

Based on a dynamical mechanical analysis, we identify the effect of lactates and octanoic acid used as external plasticizers on relaxation peaks. DMA spectra of samples containing 5 to 70 wt% of plasticizer were compared to one another.

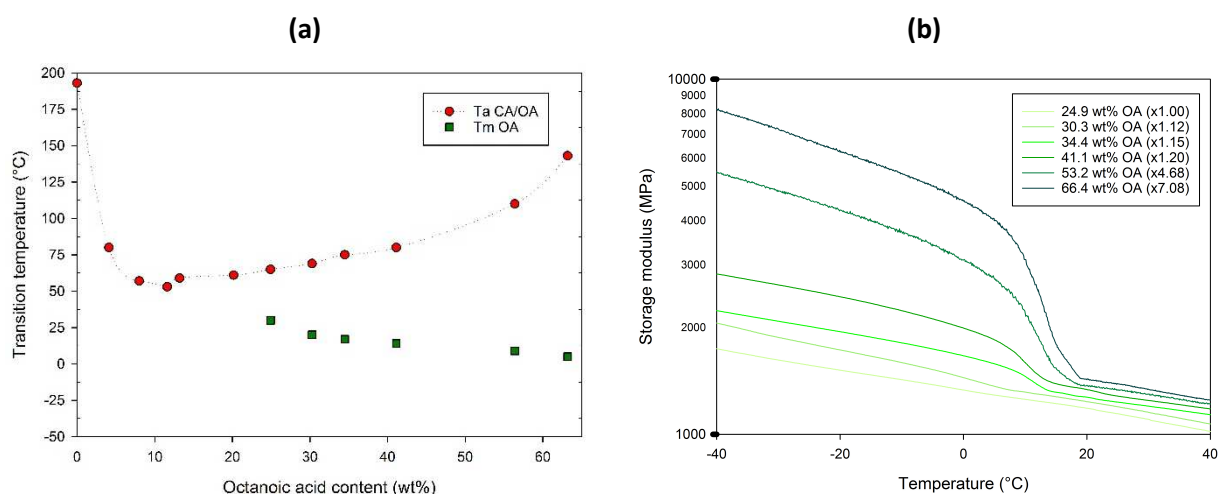


Figure 1: (a) Transition temperatures of CA/OA blends, according to the real plasticizers content. (b) Storage modulus measured at 1Hz according to temperature for CA mixtures containing different OA real content.

Thermal properties of CA / OA tested samples were investigated by DMA. Results were presented in Fig. 1a. With low amounts of octanoic acid as plasticizer, a decrease in α relaxation temperature could be observed, which is considered as the glass transition temperature of the system. The Tg decreased around 50°C with less than 10 wt% of OA. At low rate, OA was a very good plasticizer of the CA system. With plasticizer rates higher than 25 wt%, the Tg of the blends CA / OA shifted to high temperatures.

According to storage modulus curves (Fig. 1b), all the cellulose acetate blends containing between 25 to 66 wt% of OA remained unmixed. In fact, all of them presented a drop around 17 °C which increase with the OA content. This drop can be attributed to the melting temperature of pure OA

(Inoue, Hisatsugu, Suzuki, Wang, & Zheng, 2004), indicating that, a phase separation occurred in the blend (between CA and OA). The extent of the drop around 17 °C increases with the OA content. The quantity of OA that has demixed, which does not plasticize CA chains, increased. It seemed that after a definite composition, between 20 wt% and 25 wt%, octanoic acid which was added to the mixture led to the formation of a two-phase system with an OA-pure phase. The increase of T_g for increasing OA content suggests that some of the OA which plasticized CA at lower concentration could migrate to the OA -pure phase. That is to say, additional acid had more affinity with the pure OA phase than with CA / OA phase, and as consequence, less octanoic acid was available for the plasticization of CA chains.

This demixing phenomenon of octanoic acid could be confirmed by SEM (Fig. 2). The sample containing about 20 wt% of octanoic acid had a completely homogeneous surface, while the sample containing 40 wt% of OA shows a porous structure.

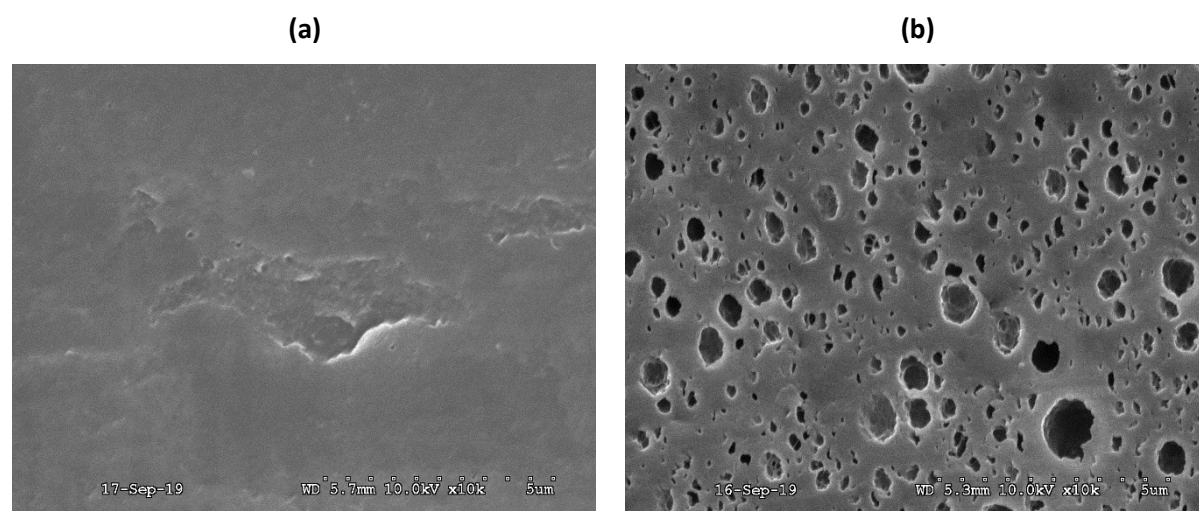


Figure 2 : Scanning electron micrographs X 10 000 from the prepared surfaces of cellulose acetate blends containing (a) 20.2 wt% of OA and (b) 41.1 wt% of OA.

Fig. 3 show the variation of the T_g of CA / lactates blends obtained by DMA at a frequency of 1 Hz as a function of the lactates content, for CA / BL and CA / ELL blends respectively. On these graphs, the experimental values of the glass transition temperature could be fitted by the Fox equation (Fox, 1956).

$$1/T_{g,b} = \sum w_i/T_{g,i} \quad (1)$$

Where T_{g,b} and T_{g,i} are respectively the glass transition temperature of the blend and of the components (CA and plasticizers), and w_i is the mass fraction of component i.

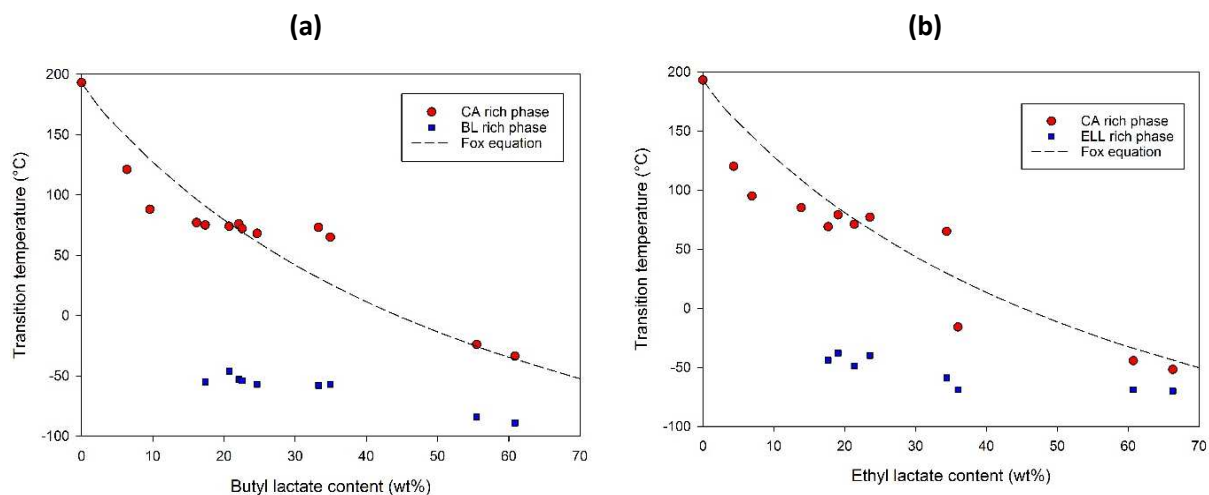


Figure 3 : Transition temperatures of (a) CA/BL blends (b) CA/ELL blends, according to the real plasticizers content.

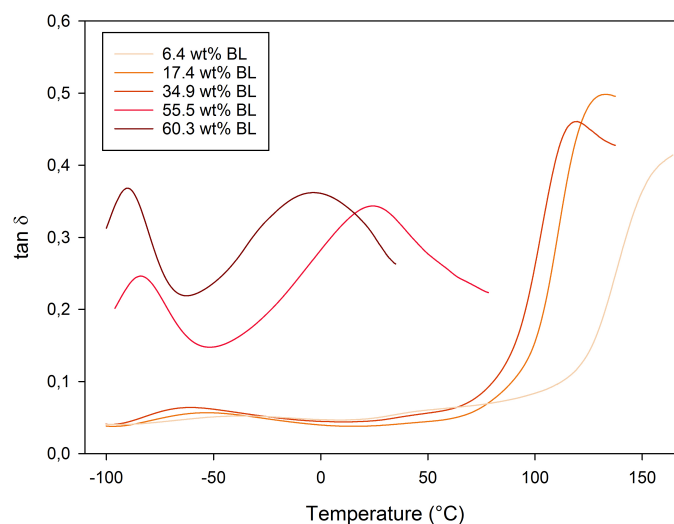


Figure 4: Tan δ measured at 1Hz according to temperature for CA mixtures containing different real BL content.

By measuring the glass transition temperature by DMA, it was possible to make a first characterization of the miscibility range of cellulose acetate / lactates blends.

It can clearly be seen that for lactates content up to 20 wt %, a single transition is found, which suggests that the mixture is monophasic and that its components are completely miscible. This transition corresponds to the glass transition of the blend which decreased first, with the increasing plasticizer contents. The reduction of T_g of cellulose acetate related to the effect of external plasticization has already been shown (Liu et al., 2006; Vidéki et al., 2007).

For lactates contents higher than 20 wt %, a second transition was found at lower temperature. It was pointed out that two phases of CA / plasticizer mixtures could be observed. The amplitude of this second relaxation increased with plasticizers rate (Fig. 4). It was possible to differentiate it from cellulose acetate β secondary relaxation, because it shifted to lower temperatures, thus introducing the concept of rich phases in cellulose acetate and rich phases in plasticizer (Bao et al., 2015; Kawai & Hagura, 2012). Other descriptions are found in the literature, assuming a complete and homogeneous miscibility of the plasticizer in the matrix. The secondary relaxation of the mixture would be due to specific polymer/plasticizer interactions (Seymour et al., 1979) or be produced by diluted chain movements in the plasticizer (Scandola & Ceccorulli, 1985b).

When it was possible to observe the relaxation of the plasticizer rich phase, a plateau around 75 °C for the relaxation of rich CA phase occurred. In other words, the transition temperature of this phase no longer decreased. For these blends compositions, values are not predicted correctly by Fox modelling.

Subsequently, with increasing amounts of lactates, experimental transitions got closer to the values obtained by the Fox equation. The two relaxations then had an equivalent intensity.

The Fox equation assumes no specific interactions between components of the mixture, such as hydrogen bonds (which preponderate in CA/lactates blends). The observed deviations can be also explained by this fact.

3.2 Thermo-mechanical properties of systems

Dynamical mechanical analysis of CA / lactate blends also allowed studying the glassy zone modulus as a function of plasticizers rate. It was summarized in Fig. 5.

For blending compositions with 0 to 10 wt% of plasticizer in which there was a decrease in α

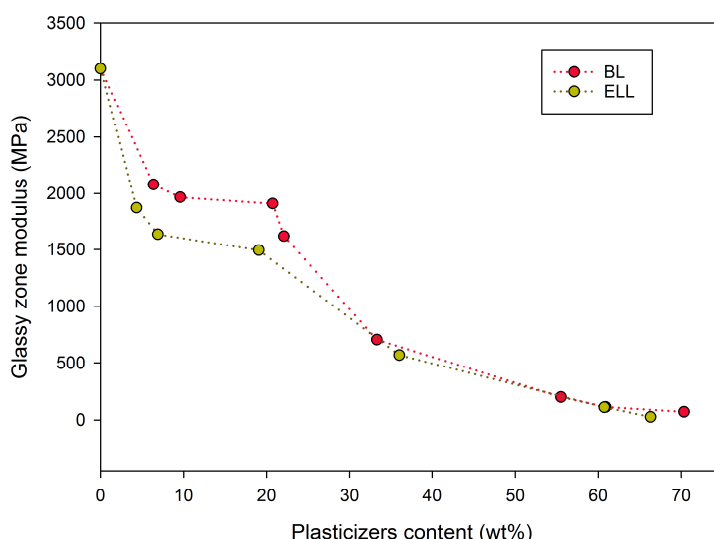


Figure 1: Glassy zone modulus temperature of CA/BL and CA/ELL blends, according to the real plasticizers content.

transition, a drop of the glassy zone modulus plateau was also observed. For concentrations of plasticizers above 10 wt%, composition at which a plasticizer rich phase appears, the glassy zone modulus stabilizes. Above 20 wt% of plasticizers, a second modulus drop appeared. According to Fig. 7 crystallinity vanished at the same rate. A second modulus plateau was perceived next to 50 wt%. This last one could be analysed as cellulose acetate chains diluted in lactates, which were then a major part in the blend.

3.3 Effect of plasticizer on the crystallinity and molecular organization.

It is known that cellulose acetate is a partially crystalline polymer and transition from the glassy to the rubbery state is due to amorphous fractions of polymers. Scandola M. and al. (Scandola & Ceccorulli, 1985b) have hypothesized that small amounts of plasticizers only solvate the amorphous regions. To solvate the crystalline fraction of the polymer, higher amounts need to be used. They have also assumed that the whole sample could be uniformly diluted, owing to complete solvation of the crystalline fraction.

According to this, they hypothesized that if cellulose acetate retained its crystallinity after adding a small content of plasticizer, the composition of amorphous regions of cellulose acetate should be different from the nominal composition of the mixture. Given that it is amorphous regions that influence the glass transition of the blend, this may be an additional explanation to the difference with theoretical Tg values predicted by Fox equation.

The effect of plasticizers on the degree of crystallinity of cellulose acetate is briefly discussed in this section. Fig. 6 and 7 show X-ray diffraction profiles at small and wide angles of samples prepared via solvent casting method and give additional information on plasticizing effects.

The presence of periodic structures generates scattering peaks; abscissa of these peaks correspond with the average inter-domain distance also called *d*-spacing.

It can be described by:

$$d = 2\pi/q^* \quad (2)$$

where q^* is the q value corresponding to the maximum intensity in \AA^{-1} and d is the d -spacing value in \AA .

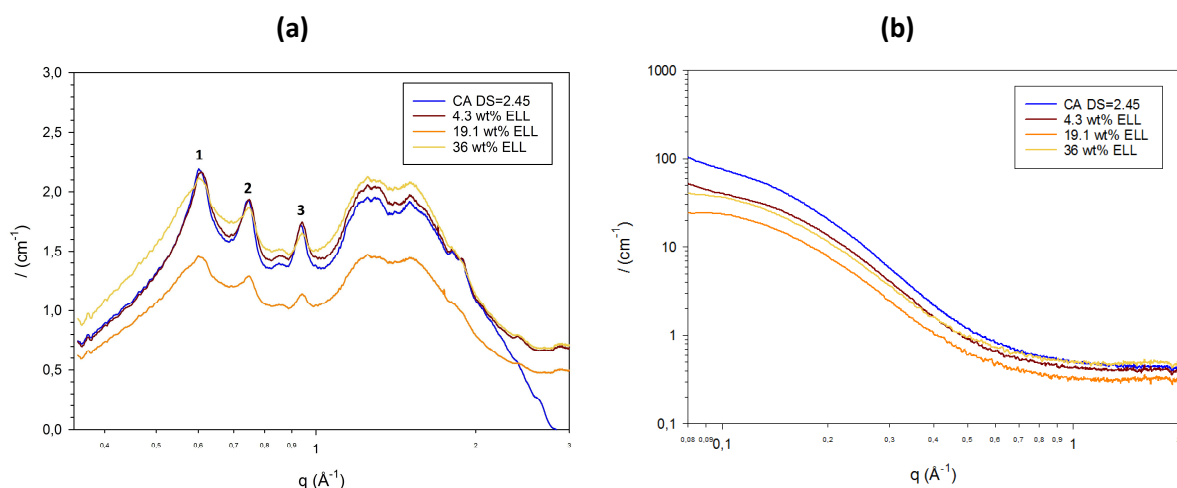


Figure 6: (a) WAXS and (b) SAXS profiles, CA/ELL blends

228

229 Fig. 6 corresponds to SAXS and WAXS profiles for CA / ELL blends. For these systems, in WAXS

230 profiles, we can clearly see that crystallinity is preserved with the addition of ELL. The three

231 characteristic crystalline peaks of unplasticized cellulose acetate can be identified. We can observe

232 them at d-spacings of $d_1=10.5$, $d_2=8.4$ and $d_3=6.8$ Å and their values are in agreement with literature

233 values (Fawcett et al., 2013; Yu BAO, 2015). Nonetheless, the intensity of the peaks decreases with

234 the increasing ELL content. SAXS curves also present the same profile, undoubtedly inherited from

235 the presence of the crystallites.

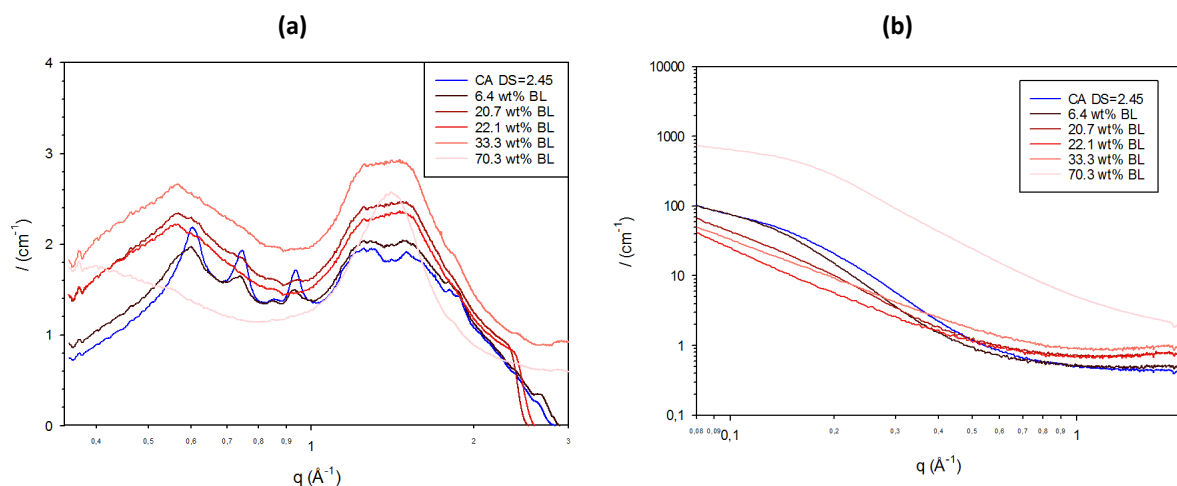


Figure 7 : (a) WAXS and (b) SAXS profiles, CA/BL blends

236

237 WAXS profiles of CA / BL systems (Fig. 7a) show an assignment of crystallinity according to the

238 composition of the blend. At BL contents larger than 20 wt%, the crystallinity is no longer visible. The

239 SAXS analysis (Fig. 7b) permits to highlight the evolution of the diffusion with blend composition. In

other words, the plasticizer has affected the structure. As seen previously, beyond 20 wt% of BL, the crystallinity was no longer observed. It may be hypothesized that the response of the amorphous phase is examined. Beyond 33 wt% the slope is affected. This suggests a more open molecular organization due to the presence of plasticizer. At 70 wt% of BL, a change appears in the profile. The hypothesis can be made that after a relatively high BL content, it acts as a solvent for the CA. The structure seems diluted.

It appears that ELL is a less active solvent than BL. We suggest that this phenomenon should be attributed to the lack of compatibility between ELL / CA, hence the ELL being rejected by the crystalline phase in the amorphous phase. Therefore the crystalline phase is not affected.

3.4 Blends behaviour and miscibility

Five different regions have been suggested during the cellulose acetate plasticization process with the increasing content of plasticizers as shown in a schematic drawing (Fig. 8). Pure CA was described as a polymer formed of short and long chains with a low degree of crystallinity (Bao et al., 2015). At low plasticizer content (region n°1), lactate molecules are mixed homogeneously with CA. The polymer amorphous phase is plasticized by the plasticizer. It leads to a decrease in Tg and glassy plateau modulus of the blend with the increasing plasticizer content. Then when the plasticizer content increases (region n°2), a portion of the plasticizer regroups to create a plasticizer-rich phase containing short CA chains (Spurlin, Martin, & Tennent, 1946) . At these compositions, blends are not totally miscible. There is a plateau for the main transition of the CA-rich phase and for the glassy zone modulus. This assumes that in this phase, the plasticizer rate does not increase or only marginally.

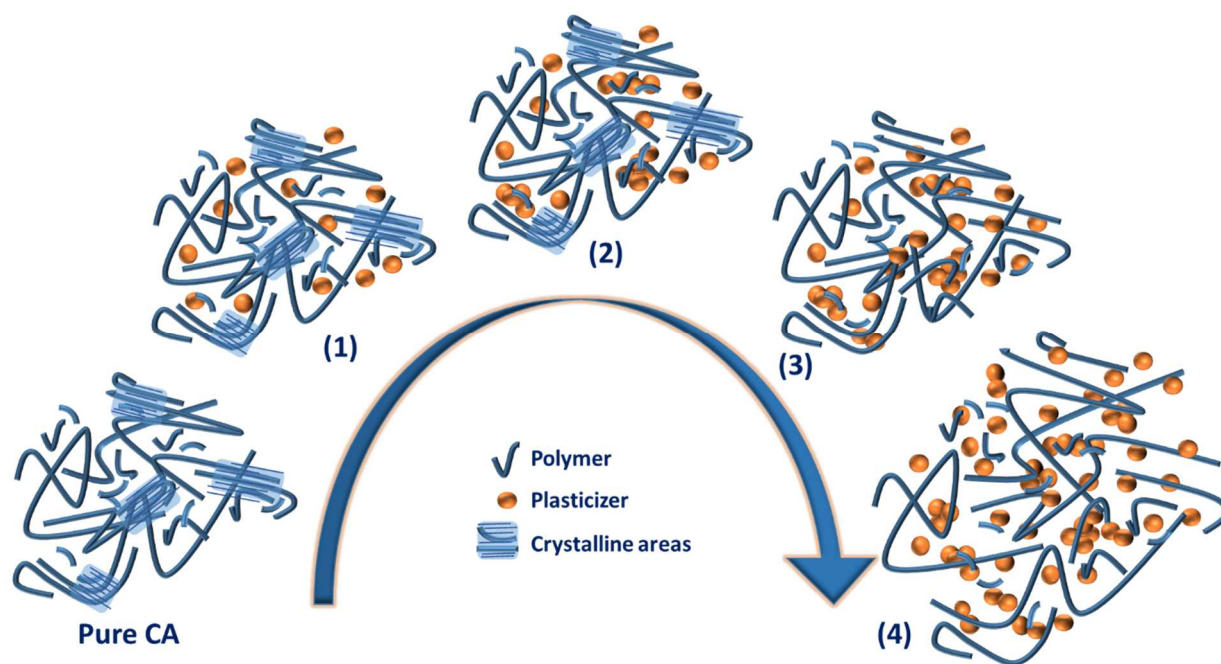


Figure 8: Schematic representation of the behaviour of cellulose acetate with the increasing plasticizer content.

With a higher plasticizer content, a modulus drop was observed and X-ray diffraction analyses have shown a disappearance of crystallinity and more spacing between CA chains, which indicates that the molecular mobility of the CA-rich phase is affected by the plasticizer (region n°3). In a mixture with even more plasticizer (region n°4), the behaviour of the blend is totally different. Short and long CA chains have been dissolved by plasticizer. The structure of the mixture is significantly more open, the plasticizer governs the molecular mobility. A possible interpretation for this behaviour is that the plasticizer-rich phase, which is scattered in the CA-rich phase, has developed enough to break intermolecular H-bonding. These hydrogen bonds may be at the origin of a closer molecular organization. A high threshold of plasticizer could eliminate them.

4. Conclusions

The dynamical properties of plasticized cellulose acetate have been examined by dynamical mechanical analysis, structural properties and crystallinity were investigated by X-ray diffraction for a more detailed description of blends. For octanoic acid, a decrease of the glass transition temperature followed by an unmixing of the system, as a function of plasticizer content, was observed. Although it is not a good plasticizer at high content, at low concentration 10 wt% allowed a drop in Tg of approximately 150 °C. Through the correlation between DMA and WAXS/SAXS results, the

plasticizing effect of lactates on cellulose acetate were studied in detail. We interpreted data and with the help of the literature, it allowed us to highlight mechanisms regarding miscibility and phase separation in the strongly H-bonded of cellulose acetate blends with the increasing plasticizer content. With low lactates in blends, only one relaxation transition was detected by DMA, it was identified as α relaxation. A decrease of this glass relaxation, as a function of plasticizer content was observed, CA/lactates blends are miscible. From 15 wt% of lactates above the miscibility limit, two relaxations were detected, introducing the concept of CA-rich phase and plasticizer-rich phase. With an increasing amount of lactates, CA/lactates blends became amorphous. The plasticizer affect the structure that it cannot affected previously, between 20 and 40 wt% of lactates, a glassy modulus drop of approximately 1500 MPa was observed. Systems with high lactate content were strongly affected by the plasticizer-rich phase, CA-rich phase and plasticizer-rich phase transitions are closer indicating the disappearance of intermolecular interactions. These three green solvents are good candidates for making plasticized cellulose acetate by extrusion because they provide a decrease in T_g , crystallinity and glassy modulus. Nevertheless octanoic acid need to be used under 30 wt%. The description of these systems need further examination for understanding the chemical mechanisms regarding miscibility and phase separation.

Acknowledgments:

The authors appreciatively thank the FUI FOR-TUNE, and more particularly Bpi France, the DGE (Directorate General for Enterprise), the Minister for Enterprises, the Auvergne Rhône-Alpes Region, and the FEDER European Funds, for their financial support and more particularly Olivier Chaubet from Solvay for the fruitful discussions. The authors also thank RHODIA Acetow for their supply of commercial cellulose acetate and Carlos Fernandez de Alba from the ICL polymeric NMR service (IMP / CNRS / UMR 5223) for his kind welcome and help. They acknowledge all the project partners.

References

- Bao, C. Y., Long, D. R., & Vergelati, C. (2015). Miscibility and dynamical properties of cellulose acetate/plasticizer systems. *Carbohydrate Polymers*, 116, 95–102. <https://doi.org/10.1016/j.carbpol.2014.07.078>
- Biańska-Florjańczyk, E., & Florjańczyk, Z. (2007). Chapter 22 - Solubility of Plasticizers, Polymers and Environmental Pollution. In T. M. Letcher (Ed.), *Thermodynamics, Solubility and Environmental Issues* (pp. 397–408). <https://doi.org/10.1016/B978-044452707-3/50024-0>
- Fawcett, T. G., Crowder, C. E., Kabekkodu, S. N., Needham, F., Kaduk, J. A., Blanton, T. N., ... Shpanchenko, R. (2013). Reference materials for the study of polymorphism and crystallinity in cellulose. *Powder Diffraction*, 28(1), 18–31. <https://doi.org/10.1017/S0885715612000930>
- Fox, T. G. (1956). Influence of Diluent and of Copolymer Composition on the Glass Temperature of a Poly-mer System. *Bull. Am. Phys. Soc.*, 1, 123.
- Inoue, T., Hisatsugu, Y., Suzuki, M., Wang, Z., & Zheng, L. (2004). Solid–liquid phase behavior of binary fatty acid mixtures: 3. Mixtures of oleic acid with capric acid (decanoic acid) and caprylic acid (octanoic acid). *Chemistry and Physics of Lipids*, 132(2), 225–234. <https://doi.org/10.1016/j.chemphyslip.2004.07.004>
- Kamide, K., & Saito, M. (1985). Thermal Analysis of Cellulose Acetate Solids with Total Degrees of Substitution of 0.49, 1.75, 2.46, and 2.92. *Polymer Journal*, 17(8), 919–928. <https://doi.org/10.1295/polymj.17.919>
- Kawai, K., & Hagura, Y. (2012). Discontinuous and heterogeneous glass transition behavior of carbohydrate polymer–plasticizer systems. *Carbohydrate Polymers*, 89(3), 836–841. <https://doi.org/10.1016/j.carbpol.2012.04.018>
- Lee, D. H., Lee, J. H., Cho, M. S., Choi, S. H., Lee, Y. K., & Nam, J. D. (2005). Viscoelastic characteristics of plasticized cellulose nanocomposites. *Journal of Polymer Science Part B: Polymer Physics*, 43(1), 59–65. <https://doi.org/10.1002/polb.20307>

- Liu, C., He, J., Ruymbeke, E. van, Keunings, R., & Bailly, C. (2006). Evaluation of different methods for the determination of the plateau modulus and the entanglement molecular weight. *Polymer*, 47(13), 4461–4479. <https://doi.org/10.1016/j.polymer.2006.04.054>
- Lizhi, H., Toyoda, K., & Ihara, I. (2008). Dielectric properties of edible oils and fatty acids as a function of frequency, temperature, moisture and composition. *Journal of Food Engineering*, 88(2), 151–158. <https://doi.org/10.1016/j.jfoodeng.2007.12.035>
- Lomba, L., Giner, B., Zuriaga, E., Gascón, I., & Lafuente, C. (2014). Thermophysical properties of lactates. *Thermochimica Acta*, 575, 305–312. <https://doi.org/10.1016/j.tca.2013.11.010>
- McBrierty, V. J., Keely, C. M., Coyle, F. M., Xu, H., & Vij, J. K. (1996). Hydration and plasticization effects in cellulose acetate: molecular motion and relaxation. *Faraday Discussions*, 103, 255–268. <https://doi.org/10.1039/FD9960300255>
- Nair, M. K. M., Joy, J., Vasudevan, P., Hinckley, L., Hoagland, T. A., & Venkitanarayanan, K. S. (2005). Antibacterial Effect of Caprylic Acid and Monocaprylin on Major Bacterial Mastitis Pathogens. *Journal of Dairy Science*, 88(10), 3488–3495. [https://doi.org/10.3168/jds.S0022-0302\(05\)73033-2](https://doi.org/10.3168/jds.S0022-0302(05)73033-2)
- Pereira, C. S. M., Silva, V. M. T. M., & Rodrigues, A. E. (2011). Ethyl lactate as a solvent: Properties, applications and production processes – a review. *Green Chemistry*, 13(10), 2658–2671. <https://doi.org/10.1039/C1GC15523G>
- Quintana, R., Persenaire, O., Lemmouchi, Y., Bonnaud, L., & Dubois, P. (2014). Grafted d/l-lactide to cellulose acetate by reactive melt processing: Its role as CA/PLA blend compatibilizer. *European Polymer Journal*, 57, 30–36. <https://doi.org/10.1016/j.eurpolymj.2014.05.003>
- Rahman, M., & Brazel, C. S. (2004). The plasticizer market: an assessment of traditional plasticizers and research trends to meet new challenges. *Progress in Polymer Science*, 29(12), 1223–1248. <https://doi.org/10.1016/j.progpolymsci.2004.10.001>
- Scandola, M., & Ceccorulli, G. (1985a). Viscoelastic properties of cellulose derivatives: 1. Cellulose acetate. *Polymer*, 26(13), 1953–1957. [https://doi.org/10.1016/0032-3861\(85\)90173-9](https://doi.org/10.1016/0032-3861(85)90173-9)

- Scandola, M., & Ceccorulli, G. (1985b). Viscoelastic properties of cellulose derivatives: 2. Effect of diethylphthalate on the dynamic mechanical relaxations of cellulose acetate. *Polymer*, 26(13), 1958–1962. [https://doi.org/10.1016/0032-3861\(85\)90174-0](https://doi.org/10.1016/0032-3861(85)90174-0)
- Seymour, R. W., Weinhold, S., & Haynes, S. K. (1979). Mechanical and dielectric relaxation in cellulose esters. *Journal of Macromolecular Science, Part B*, 16(3), 337–353. <https://doi.org/10.1080/00222347908212300>
- Spurlin, H. M., Martin, A. F., & Tennent, H. G. (1946). Characterization of cellulose derivatives by solution properties: Plasticizers as solvents. *Journal of Polymer Science*, 1(2), 63–74. <https://doi.org/10.1002/pol.1946.120010201>
- Vidéki, B., Klébert, S., & Pukánszky, B. (2007). External and internal plasticization of cellulose acetate with caprolactone: Structure and properties. *Journal of Polymer Science Part B: Polymer Physics*, 45(8), 873–883. <https://doi.org/10.1002/polb.21121>
- Vieira, M. G. A., da Silva, M. A., dos Santos, L. O., & Beppu, M. M. (2011). Natural-based plasticizers and biopolymer films: A review. *European Polymer Journal*, 47(3), 254–263. <https://doi.org/10.1016/j.eurpolymj.2010.12.011>
- Wu, J., Zhang, J., Zhang, H., He, J., Ren, Q., & Guo, M. (2004). Homogeneous acetylation of cellulose in a new ionic liquid. *Biomacromolecules*, 5(2), 266–268. <https://doi.org/10.1021/bm034398d>
- Wypych, G. (Ed.). (2012). 10 - EFFECT OF PLASTICIZERS ON PROPERTIES OF PLASTICIZED MATERIALS. In *Handbook of Plasticizers (Second Edition)* (pp. 209–306). <https://doi.org/10.1016/B978-1-895198-50-8.50012-6>
- Wypych, G. (2017). *Handbook of Plasticizers*. Elsevier.
- Yu BAO, Y. B. (2015). *Cellulose acetate/plasticizer systems: structure, morphology and dynamics*. Universite Claude Bernard - Lyon I.