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Xavier Dreux[a], Jean-Charles Majesté[a], Christian Carrot[a], Alexandra Argoud[b], Caroll Vergelati[b]

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

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

E-mail addresses :

xavier.dreux@univ-st-etienne.fr (X. Dreux)

majeste@univ-st-etienne.fr (JC. Majesté) Corresponding author

carrot@univ-st-etienne.fr (C. Carrot)

alexandra.argoud@solvay.com (A. Argoud)

caroll.vergelati@solvay.com (C. Vergelati)

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Abstract

The viscoelastic behaviour of cellulose acetate with a degree of substitution (DS) of 2,45 plasticized by triacetin was studied at short times by dynamic oscillatory measurements. Two distinct regimes and unexpected scaling behaviour according to plasticizer content were highlighted. The dynamics of chains and their structural organization are not modified up to 35wt% of triacetin. The rheological behaviour is led by a constant correlation length corresponding to the distance between strong intermolecular interactions subsisting in the melt state at high temperature even in the presence of plasticizer. This particular structure involves the apparition of strain hardening effects during uniaxial extensional flow tests and an important elasticity corresponding to the apparition of a Weissenberg effect at really low shear rates during shear sweeps. Intramolecular hydrogen bonds are responsible of the high rigidity of cellulose acetate chains. Plasticized cellulose acetate in the melt state belongs to the class of associating polymers and its rheological behaviour is mainly led by stickers.

Keywords : *Cellulose acetate, plasticizer, rheology, viscoelasticity, dynamics of chains, intermolecular interactions*

1. Introduction

Among cellulose derivatives, cellulose acetate (CA) is the most widely produced ester for thermoplastic applications (Balser et al., 2004; Ganster & Fink, 2013). In this case, hydroxyl groups of anhydroglucopyranose (AGU) units that compose cellulose are replaced by acetyl groups during an acetylation process. Cellulose acetate properties depend on the degree of substitution (DS)

corresponding to the average number of hydroxyl groups replaced in an AGU unit. The melt processing of CA is possible only for a degree of substitution close to 2,5 (Kamide & Saito, 1985). Even in this cases, the temperature window for processing is narrow because the glass transition temperature (Tg) is close to the decomposition temperature (Mohanty, Wibowo, Misra, & Drzal, 2003; Quintana, Persenaire, Bonnaud, & Dubois, 2012). In order to facilitate the transformation in the melt state, external plasticization with low molecular weight plasticizers is a common solution (B. Wang et al., 2016; Zepnik, Kabasci, Kopitzky, Radusch, & Wodke, 2013).

The use of eco-friendly plasticizer as triacetin (TA) rather than widely used phthalate plasticizers is necessary for the development of cellulose acetate based materials (Wypych, 2017). The usual plasticizer content mixed with cellulose acetate is generally between 15 and 35wt% in the different applications to optimize both process and final mechanical properties (Balser et al., 2004; Ganster & Fink, 2013). However, miscibility for the CA/TA mixture is not achieved over the whole range of composition. Some previous study (C. Bao, 2015) have shown by means of modulated DSC (MDSC), dynamic mechanical analysis in temperature (DMTA) and neutron scattering at small angles (SANS) that in the case of triacetin, phase separation occurs for 20 wt% TA introduced in bulk cellulose acetate (25 wt% for DEP). Then, two phases are observed, one considered as rich in CA and a second one, rich in plasticizer. Phase separation and partial miscibility results in a double Tg behavior for TA content above 20 wt%. For CA-rich phase the decrement of Tg is clearly significant (up to -200 °C). For TA-rich phase, Tg is weakly dependent on the composition and close to that of the plasticizer.

Cellulose acetate chains have an important rigidity and are considered as semiflexible or even inflexible because of residual intramolecular hydrogen bonds within a chain despite the esterification reaction (Hsieh & Kadla, 2012; Kawanishi, Tsunashima, Okada, & Horii, 1998; B. Wang et al., 2016). Its persistence length is maximum for DS close to 2,5 and constituted of 19 AGU units which correspond to 10 nm (Kamide, 2005a). Moreover, in the solid state, the distance between two neighboring chains is estimated around 1 nm because of residual intermolecular hydrogen bonds formed by free hydroxyl groups along chains (C. Bao, 2015). The existence of interactions between OH side groups of different chains is highlighted by several studies (Kamide, 2005b; Puleo, Paul, & Kelley, 1989).

The rheological behaviour of cellulose acetate in solution has been widely studied for different solvents (Ferrarezi, Rodrigues, Felisberti, & Gonçalves, 2013; Kawanishi, Tsunashima, & Horii, 2000; C. S. Wang & Fried, 1992). However, to the best of our knowledge, there are surprisingly very few studies that analyzed the viscoelastic behaviour of plasticized cellulose in the melt state and therefore for cellulose acetate / triacetin blends. The viscoelastic properties of cellulose acetate of DS 2,5 plasticized by 15wt% of triacetin or triethyl citrate (TEC) were studied by Small Amplitude Oscillatory Shear (SAOS). Similar curves were obtained for both plasticizer and shown typical shear thinning behaviour. According to the authors, "*externally plasticized cellulose acetate shows a rheological behaviour typical for conventional thermoplastics*" (Erdmann, Kabasci, Kurek, & Zepnik, 2014). Additional study investigated rheological behaviour at large deformations and high shear rates (Zepnik et al., 2013). The shear viscosity of cellulose acetate / TEC systems as a function of shear rate was studied at 220°C for plasticizer contents of 15, 20 and 25wt%. The authors reported that it is possible to produce a master curve thanks to a concentration-dependent shift factor. Under uniaxial extensional flow, a strain hardening effect was highlighted for the three TEC contents for low strain. In their case, an increasing amount of plasticizer shifts the maximum of the strain hardening to higher extension rates. Then, there is an elongational thinning region which is independent from TEC concentration. However, the authors did not underline the particularity of the strain hardening effect that occurred whatever the TEC content was.

According to the few results available in the literature, the presence of intermolecular and intramolecular interactions between cellulose acetate chains is highlighted in solution but was not reported at high temperature in the melt state. The aim of this paper is to study the effect of the plasticizer content on the viscoelastic behaviour and the structural organization of cellulose acetate/triacetin blends in the melt state. To do that, viscoelasticity of plasticized cellulose acetate was characterized both in linear and nonlinear domains to determine whether or not interactions still remain in the melt state despite the presence of plasticizer. Moreover, because there is no study reporting this in the literature, the effects on the chains dynamics and flow behaviour of cellulose acetate for different triacetin contents has been investigated over the complete phase diagram.

2. Experimental section

2.1 Materials

Cellulose acetate (powder, Mw = 93 000 g/mol and polydispersity index of 2,2) with a degree of substitution of 2,45 was supplied by Acetow GmbH (Freiburg, Germany). Triacetin (TA) (purity ≥ 99,5%) was produced by Lanxess (Köln, Germany). Diethyl phthalate (DEP) whose grade is Provichem 1622 (purity ≥ 99,5%) was purchased from Proviron (Oostende, Belgium) and used as a reference (Table 1). Samples with plasticizer content from 0 to 100wt% were prepared to study the complete phase diagram.

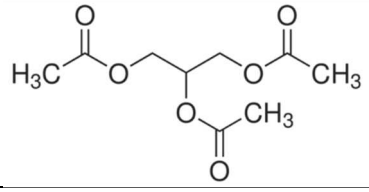
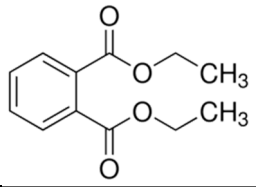
Properties	**Triacetin (TA)**	**Diethylphtalate (DEP)**
CAS number	102-76-1	84-66-2
Chemical formula	$C_9H_{14}O_6$	$C_{12}H_{14}O_4$
Chemical structure		
Molar mass (g/mol)	218	222
$T_{boiling}$ (°C)	260	298
Density (at 25°C)	1,16	1,12
Tg (°C)	-70	-88

Table 1 : Properties of plasticizers

The plasticizer contents were controlled and validated by ^{1}H NMR spectroscopy measurements. The analysis solvent was acetone-d_6 (purity ≥ 99%) and pyrrole (purity ≥ 99%) was used as a reference to quantify the plasticizer content by weight thanks to a comparative method. They were both supplied by Acros Organics (Geel, Belgium). Measurements were carried out with a Bruker AVANCE III 400MHz spectrometer.

2.2 Sample preparation

Cellulose acetate powder was dried at 70°C for at least 24h before processing. Two complementary methods were used to manufacture films of plasticized cellulose acetate. Melt processing was used for samples up to 35wt% of plasticizer while solvent casting method has been chosen above this content to overcome extrusion limitations. Films thickness was set between 0,5mm and 1mm to optimize samples for rheological measurements. The effect of processing method has been investigated for samples with 10, 20 and 35wt%.

2.2.1 Melt processing

A co-rotating twin screw extruder Leistritz ZSE 18 MAXX was used to incorporate plasticizer for melt processing up to 35wt%. The screw diameter (D) was 18mm and the screw length was 44 D. A flat die was used to produce films. The injection of the liquid plasticizer was first done with a peristaltic pump and cellulose acetate powder was added thanks to a lateral hopper. The screw speed and the temperature were adapted according to the plasticizer content from 150 rpm and 220°C at 10wt% of plasticizer to 200 rpm and 175°C at 35wt% of plasticizer.

2.2.2 Solvent casting method

Regarding the casting method, cellulose acetate and plasticizer were dissolved in acetone at a concentration of 10wt%. Acetone is an efficient and common solvent for cellulose acetate with DS of 2,45 and presents the advantage to be volatile for the solvent casting method. The solutions were mixed for 24h at room temperature thanks to a magnetic stirring bar. After this step, the solutions were poured in a PTFE mold closed with a glass upper part drilled on the top in order to control the slow evaporation of acetone. This device was optimized by former works (C. Y. Bao, Long, & Vergelati, 2015). The evaporation time depends on the plasticizer content.

2.3 Characterization methods

2.3.1 Shear rheology tests

The linear viscoelastic properties were measured with a TA Instruments ARES or ARES G2 rheometer equipped with stainless-steel parallel plates of diameter 8 or 25 mm according to the material compliance (8 mm diameter for measurements from 0 to 35wt% of plasticizer, 25mm diameter for measurement from 50 to 90wt% of plasticizer). Small amplitude oscillation shear (SAOS) experiments were performed from 100 to 0,1 rad/s at fixed strain amplitude well within the linear regime, at different temperatures according to the plasticizer content ~~(Table 2)~~. Master-curves were built from several frequency sweeps and using the time-temperature superposition (TTS).

For samples with plasticizers contents between 10 and 35wt%, a gas convection oven has been used to reach the experimental temperature range (from 120 to 220°C). To prevent the loss of plasticizer

from the sample by evaporation, the samples were protected by a bell cover that ensure saturation of the environment with plasticizer vapour (Wee & Mackley, 1998). Regarding samples containing higher plasticizer contents, the experimental temperature range (from -10 to 100°C) allows the use of a Peltier system (APS) without bell cover considering the natural limitation of drying effects for such system.

Shear sweeps test were also performed for samples containing up to 35wt% of triacetin. Grooved parallel plates have been used in order to limit slippage (grooved cone-plate was not available). Then, it is worth to note that, as no Rabinowitsch corrections (Rabinowitsch, 1929) have been applied to the results, the following results are only qualitative and will be discussed for comparison purpose only.

2.3.2 Uniaxial extensional tests

For samples containing up to 35wt% of plasticizer, the transient uniaxial extensional viscosity was measured with a Sentmanat Extension Rheometer (SER) extensional rheology system mounted on an Anton Paar MCR 301 rheometer. The measurements were performed at 180°C for different extensional-strain rate ($\dot{\varepsilon}$) from 0,03 s^{-1} to 1 s^{-1}. Before each test starting, samples were previously conditioned several minutes at the measurement temperature in order to homogenize its temperature.

2.3.3 Measurement of the glass transition temperature

According to the triacetin content, two complementary methods have been used to determine the glass transition temperature (Tg).

Glass transitions of the samples with plasticizer content up to 35wt% were determined by differential scanning calorimetry (TA Instruments Q10). Around 5 to 10 mg of plasticized cellulose acetate was analyzed. In accordance with previous studies, heating rate of 10°C/min was applied from -80 to 160°C (Kamide & Saito, 1985; McBrierty, Keely, Coyle, Xu, & Vij, 1996; Sousa et al., 2010). Glass transition temperatures were determined from the second heat so as to suppress the influence of thermal history. An average was done with at least 3 measurements.

For better accuracy, dynamic mechanical thermal analysis was preferred for plasticizer amount above 35wt%. The glass transition temperatures were determined with a TA Instruments ARES rheometer equipped with a nitrogen tank by applying temperature sweeps at cooling rate of 4°C/min and at a frequency of 1 rad/s within the linear domain. An average was done with at least 5 measurements. The results were analyzed and used in the light of a former study that determined the glass transition temperature of phases with high content of plasticizer by modulated differential scanning calorimetry (MDSC) (C. Bao, 2015).

3. Results and discussion

3.1 Evolution of rheological parameters according to triacetin content

The viscoelastic behaviour of cellulose acetate plasticized by triacetin was studied at short times by dynamic oscillatory measurements. Master curves were obtained for samples containing between 10 and 90wt% of plasticizer (Figure 1). A reference temperature of 100°C was chosen to compare the different samples. One can notice that the rubber plateau is not clearly defined suggesting a certain polydispersity and strong coupling from the glass transition zone to the terminal zone. Whatever the triacetin content is, the shape of complex relaxation modulus seems quite classical. Then, in the following, main viscoelastic parameters have been inferred from the master curves and have been analyzed in more detail as a function of the polymer content for figure 2 and figure 3 to analyse the scaling behaviour.

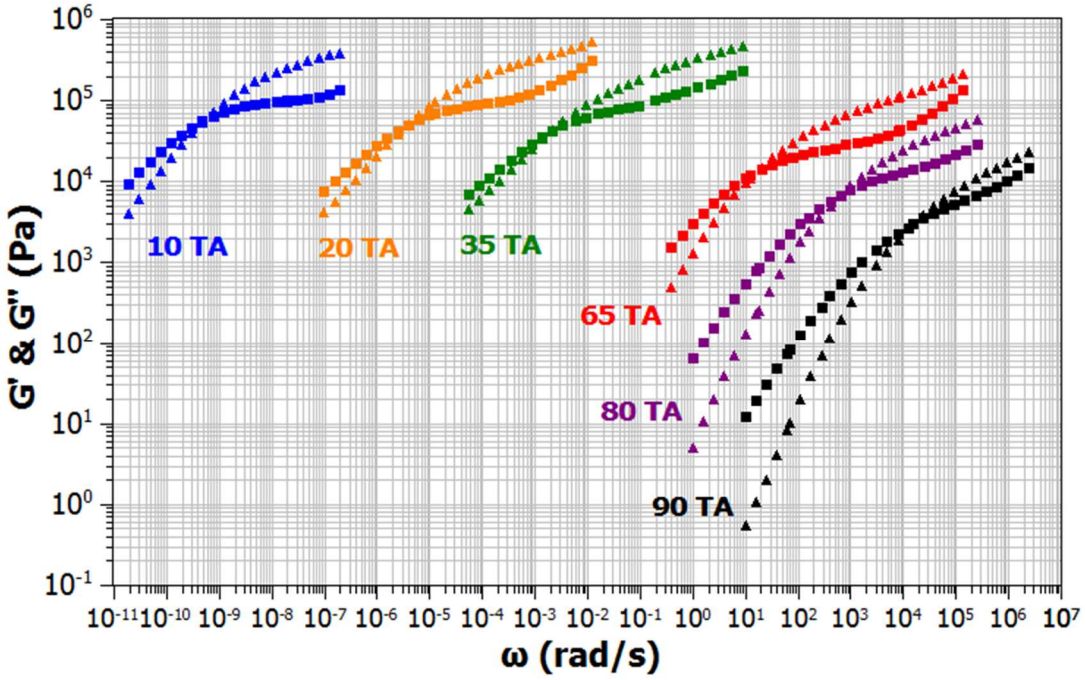


Figure 1 : Comparison of master curves at 100°C as a function of triacetin content with G' (▲) and G'' (■).

3.1.1 Rubber plateau modulus

The rubber plateau modulus G_N^0 is determined at the minimum of the damping factor tan δ (Liu, He, Ruymbeke, Keunings, & Bailly, 2006).

$$G^0_{N_{exp}} = G'(\omega)_{tan\,\delta\,min} \qquad (1)$$

Two different regimes are visible according to the triacetin content (Figure 2-a). First, up to 35wt%, the plasticizer has no significant effect on the rubber plateau modulus. Then, above 50wt% of triacetin, G_N^0 decreases in a more classical way but its value remains high even at 90wt% of triacetin where the dilute (unentangled) regime is not reached yet. Strong interactions still exist between the chains that contribute to elasticity. This fact is in agreement with some results found in the literature

concerning cellulose acetate in solution. It is worth to note that these behaviours are not related to the manufacturing processes (Figure 2). For low triacetin content up to 35%, the fact that the rubber plateau modulus remains unaffected is unexpected if the cellulose acetate chains are considered as classical linear entangled chains. This atypical result suggests that correlation lengths in tube conformation are governed by strong but labile interactions that still exist even at high temperatures and that remain unaffected up to 35wt% of triacetin. These interactions called stickers in this paper are characterized by a finite lifetime enabling connection and reconnection leading to transient network formation (Brassinne, Cadix, Wilson, & Ruymbeke, 2017). For this system, stickers may be related to strong hydrogen bonds present even in the melt state and despite the addition of plasticizer. According to the literature hydrogen bonds may subsist at high temperature. Indeed, in the case of hydroxyl-functionalized polypropylene, 50% of the hydrogen bonds initially presents were kept between chains at 250°C (Gupta et al., 2016). Moreover, for triacetin content above 35% (Figure 2-b), the plateau modulus follows scaling behaviour in $\Phi^{1,3}$ whereas $\Phi^{2 \text{ to } 2,2}$ is expected in the case of linear entangled chains in the melt state.

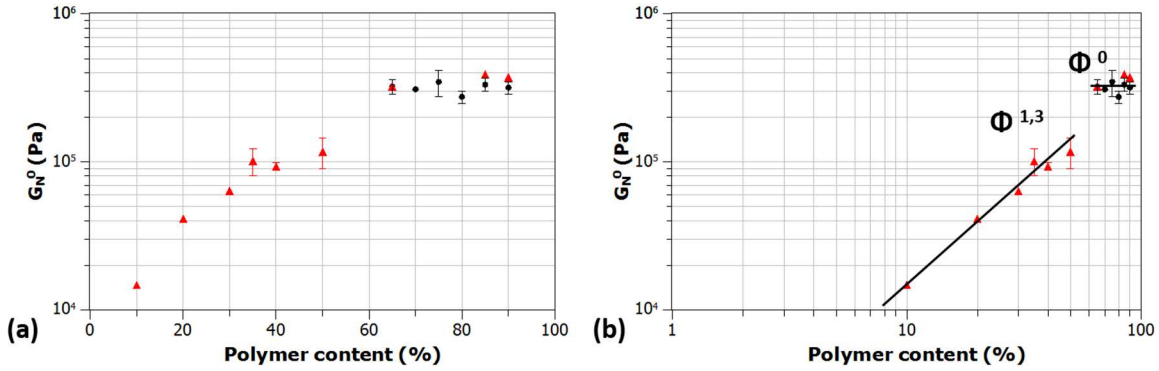


Figure 2 : Evolution of G_N^0 as a function of polymer content, lin-log plot (a) and log-log plot (b) using melt processing (●) and solvent casting (▲). Two regimes are visible, both with unexpected scaling behaviours whatever the processing method.

The same conclusions can be obtained from the evolution of the mass between entanglements (Me) inferred from the experimental value of the rubber plateau modulus $G_N^0(\Phi)$.

$$Me(\Phi) = \frac{\rho(\Phi) \times R \times T}{G_N^0(\Phi)} \qquad (2)$$

$\rho(\Phi)$ is the density according to the polymer content and calculated by a linear law of mixture. Because of the weak variation of the density when plasticizer is added, the polymer volume fraction (Φ) and mass fraction (W) are assumed to be similar. R is the ideal gas constant, and T is the temperature in K.

The mass between entanglements is rather stable or slightly decreasing up to 35wt% of triacetin. Above this value, this correlation length increases with a scaling exponent of -0,4 which is clearly different from -1 to -1,2 expected for linear entangled chains. Because of the presence of strong interactions between neighboring cellulose acetate chains, this correlation length rather corresponds to a mass between stickers (Ms) than a mass between entanglements. However, above a critical triacetin content, it seems that the plasticizer is physically able to suppress some interaction but the chains dynamics still not controlled by entanglements.

3.1.2 Relaxation times

The relaxation time (λ_n) retained to compare the different samples is related to the low frequency crossover point of G' and G'' that corresponds to shortest relaxation times in the terminal relaxation spectrum:

$$\lambda_n = \frac{\eta_0}{G_N^0} \qquad (3)$$

where η_0 is the newtonian viscosity.

To analyze the global dynamics of the plasticized cellulose acetate chains, it is necessary to overcome the strong effect of the plasticizer on the dynamics at the monomer scale. Thus, in order to compare all the samples at the same free volume (or at the same local dynamics), the relaxation times associated are analyzed at the same distance to the Tg (Tg+60°C) (Figure 3-a).

As for G_N^0, two distinct regimes are visible. Up to 35wt% of triacetin, the relaxation times remains constant whatever the triacetin content is. Despite the efforts made to have a fine repeatability for the acquisition of the data, there is still some noise mainly due to the accuracy on glass transition measurement. However, there is a noteworthy difference of behaviour compared to the samples with plasticizer contents above 60wt%. For contents lower than 35wt%, there is no effect of the triacetin on the relaxation times and on the global dynamics of the chains. The mechanisms are similar whatever the triacetin content is at the scale of the whole chains at short times. When the triacetin content exceeds a critical content, the relaxation times determined at iso-friction conditions evolve as $\Phi^{3,7}$ (Figure 3-b) which is straight different from the scaling law Φ^{1} observed for linear entangled chain (Watanabe, 1999). Thus, for plasticizer contents above 60wt%, an important change of the structural organization of cellulose acetate chains appears because of the excess of plasticizer which leads to the physical disruption of stickers.

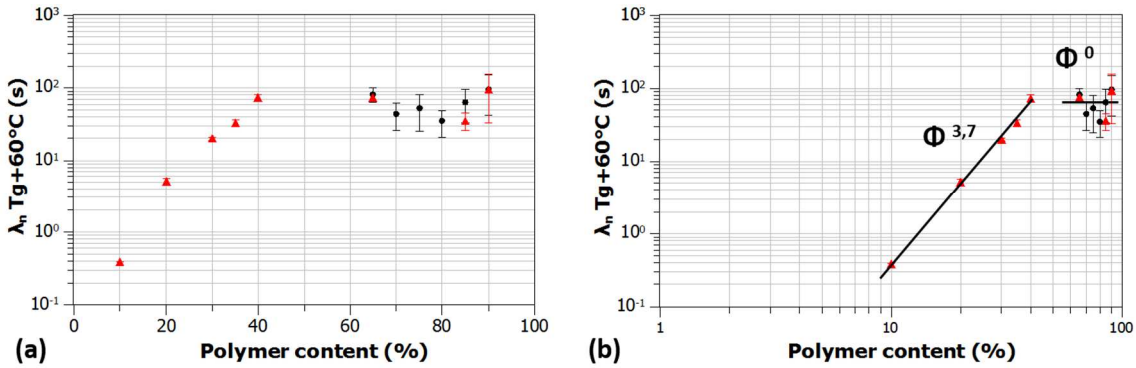


Figure 3 : Evolution of λ_n at the same distance to Tg (iso-friction conditions) as a function of polymer content lin-log plot (a) and log-log plot (b) for melt processing (●) and solvent casting (▲).

As for the rubber plateau modulus, the correlation length that controls the relaxation mechanisms is linked to the stickers. These interactions are not affected by triacetin up to 35wt% and the global chain structure is not modified. In this range of triacetin content, plasticizer seems to fill the free

volume defined between two consecutive stickers but the resulting osmotic pressure is not sufficient to unstick the chain associations. Then, the plasticizer only modifies the local environment of the chains at the monomer scale but no change in the structure and in the global dynamics at the scale of the bulk is observed. Rheological parameters depending on the whole chain dynamics remain unaffected up to the critical content of 35wt%. Above this value, the constant correlation length cannot be held.

3.2 Independence of the relaxation mechanisms at short times according to the nature of the plasticizer

The viscoelastic behaviour of extruded samples containing between 10 and 35wt% of diethyl phthalate (DEP) was studied by SAOS. The resulting master curves are then compared at the same distance to Tg with those obtained using triacetin as plasticizer. Interestingly, ~~even if the measurements were not realized within the same temperature range,~~ it seems that a unique master curve can be obtained for all the samples indifferently plasticized by triacetin or DEP (Figure 4). A similar rubber plateau is obtained no matter is the plasticizer and its concentration. None of the plasticizer has an effect on the rubber plateau modulus or its frequency span up to 35wt% of plasticizer. The nature of the plasticizer has no effect on the relaxation times at Tg+60°C. In this frequency range, global chain dynamics are mainly controlled by stickers concentration and lifetime.

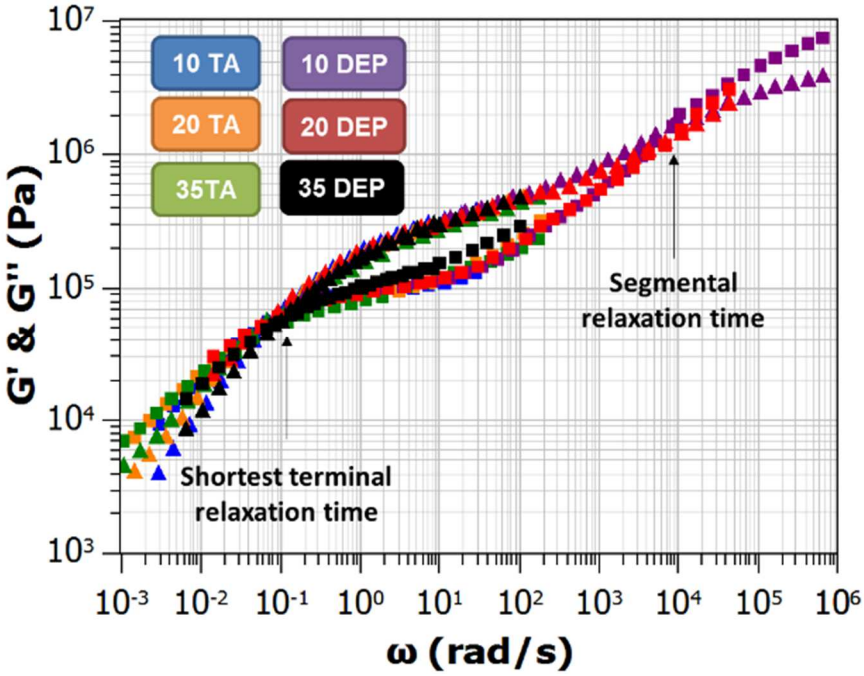


Figure 4 : Comparison of master curves at the same distance to Tg for plasticized cellulose acetate chains with triacetin or DEP contents between 10 and 35wt%.

3.3 Non-linear viscoelasticity of plasticized cellulose acetate

3.3.1 Uniaxial extensional flow at low plasticizer contents

Uniaxial extensional flow has been applied to cellulose acetate sample plasticized with triacetin contents from 10 to 35wt% (Figure 5). All the results have been compared to the Troutonian behavior (Trouton, 1906) in order to highlight the non-linearity of the transient viscoelastic response.

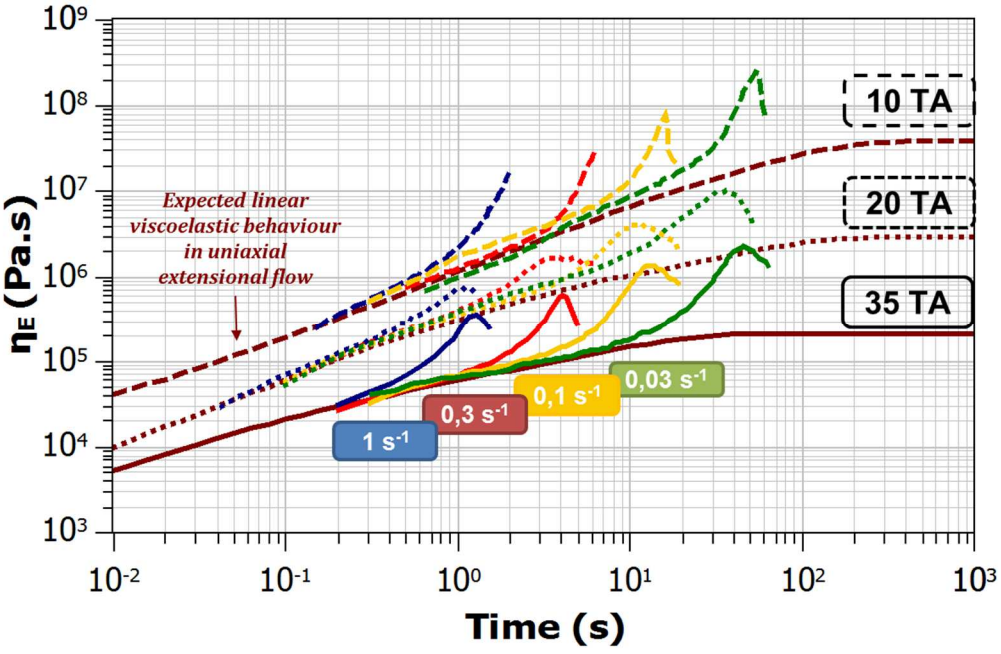


Figure 5 : Evolution of the elongational viscosity at 180°C for different $\dot{\varepsilon}$ for 10 (---), 20 (…) and 35wt% (—) of triacetin.

Whatever the triacetin content is, a clear positive deviation (namely strain hardening) from the Troutonian behaviour determined from SAOS measurements is noticed for the different extensional-strain rates. The more $\dot{\varepsilon}$ increases, the shorter is the apparition time of this strain hardening. The Troutonian viscosity decreases as a function of the triacetin content but the strain hardening effect remains noteworthy. Again, this behaviour is not consistent with simple linear entangled systems and it is possible to link it to the presence of strong interactions between cellulose acetate chains in the melt state that remains active at the time scale of the extensional test. These interactions still exist at high temperature and even for low extensional-strain rates. The presence of stickers may thus explain the apparition of the strain hardening effect in uniaxial extensional flow. During stickers "close state" lifetime, active elastic segments of average mass Ms are extended in the flow direction until their maximum elasticity is reached leading to the rising of transient extensional viscosity.

This rubber like behaviour was thus compared with a Lodge model commonly used to quantify rubber elasticity in the transient regime in the melt state (Barnes, Hutton, & Walters, 1989; Bereaux, 2004; Carrot & Guillet, 2000) (Figure 6). The theoretical viscosity (η_{Lodge}) associated to the model is obtained from :

$$\eta_{Lodge}(t) = \frac{\sigma_{Lodge}(t)}{\dot{\varepsilon}(t)} \qquad (4)$$

The Lodge stress model ($\sigma_{Lodge}(t)$) is calculated from:

$$\sigma_{Lodge}(t) = \int_{-\infty}^{t} m(t-t') \times \underline{\underline{C_t}}^{-1}(t') \times dt' \qquad (5)$$

where m(t-t') stands for the memory function determined from the relaxation time spectrum (Gi, λi):

$$m(t-t') = \sum_i \frac{G_i}{\lambda_i} \times e^{-\frac{(t-t')}{\lambda_i}} \qquad (6)$$

And the Finger's tensor defined as :

$$\underline{\underline{C_t}}^{-1}(t') = \begin{bmatrix} e^{[-2(\varepsilon(t')-\varepsilon(t)]} & 0 & 0 \\ 0 & e^{\varepsilon(t')-\varepsilon(t)} & 0 \\ 0 & 0 & e^{\varepsilon(t')-\varepsilon(t)} \end{bmatrix} \qquad (7)$$

The experimental transient extensional viscosities follow pretty well the theoretical values obtained with the Lodge model up to 35wt% of triacetin whatever $\dot{\varepsilon}$ is. The strain hardening amplitude is well predicted by Lodge model. The samples containing 35wt% of triacetin had a better reproducibility. According to this result, there are certainly long-life interactions at the timescale of the test which prevent chain slippage even for the lowest $\dot{\varepsilon}$ and therefore the longest experimental time.

Because of strong intermolecular interactions between stretched cellulose acetate chains, there is no stretch relaxation of the species that should contribute to the lowering of the strain hardening as for branched entangled polymers. For samples containing 70wt% of triacetin, a weaker and unclear strain hardening is also visible (Report to supporting information).

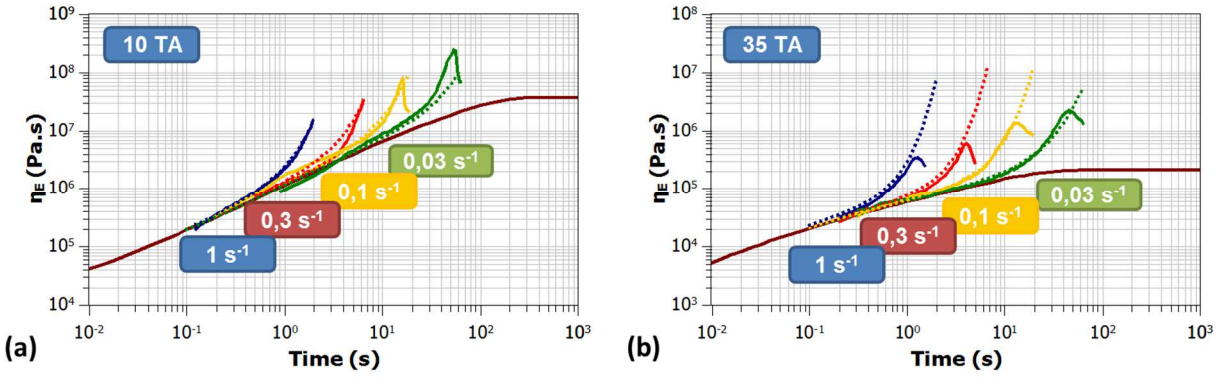


Figure 6 : Comparison of experimental elongational viscosities (—) and Lodge model (---) for 10 (a) and 35wt% of triacetin (b) at 180°C.

For better quantitative analysis, results are normalized by the Troutonian behaviour. The normalized viscosity ($\eta_{normalized}$) is :

$$\eta_{normalized} = \frac{\eta_E}{3\eta(t)} \qquad (8)$$

To suppress the effect of the elongation speed, this normalized viscosity is plotted as a function of the Hencky strain (ε_H) corresponding to :

$$\varepsilon_H = ln\frac{L}{L_0} \qquad (9)$$

It seems that the intensity of the strain hardening effect does not depend on the triacetin content (Figure 7). The values are slightly lower for 20wt%. However, the apparition of strain hardening is abrupt in all the cases and there is clearly a critical strain of the system before the starting of the strain hardening which can be estimated between 0,4 and 0,6 Hencky. Moreover, a similar limited deformation around 1 Hencky is visible whatever the triacetin content is. These results confirm that, as observed for SAOS experiments, the extensional behaviour is similar from 10 to 35wt% of plasticizer corresponding to no changes in the structure at the scale of several chains. These results suggest that, up to 35wt%, the length of active elastic segments is the same whatever the plasticizer content is.

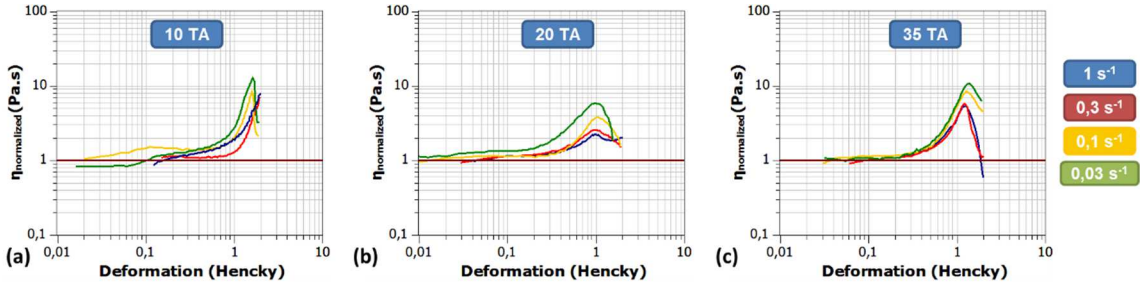


Figure 7 : Normalized viscosity as a function of the Hencky strain (ε_H) for 10wt% (a), 20wt% (b) and 35wt% (c) of triacetin at 180°C.

3.3.2 Rigidity of cellulose acetate chains

Taking advantage of the results obtained by uniaxial extensional flow, the rigidity of plasticized cellulose acetate chains has been investigated. The Flory characteristic ratio (C_∞) was estimated assuming that elastic segment between two consecutives stickers has a finite extension which is reached at the onset of the strain hardening (critical deformation, ε_c).

The theory of rubber elasticity based for crosslinked chains network was used to estimate from the critical deformation. To do that, the hypothesis that the network created by stickers is stable in the timescale of the test so that all the segments between two consecutive stickers are elastically active and confer an elastic behaviour to the system. From a definition of the entropy according to the extension ratio (λ), it is possible to use the following equation to determine the resulting stress (σ) :

$$\sigma = E\left(\lambda - \frac{1}{\lambda^2}\right) = E \times \varepsilon \qquad (10)$$

E is the Young modulus and ε is the strain. In the case of an affine and homogeneous deformation, the critical extension ratio is defined by :

$$\lambda_c = \frac{r_{max}}{r_0} \qquad (11)$$

The length r_{max} is the end to end distance of the chain segment between two consecutives stickers in fully extended configuration whereas r_0 corresponds to its equilibrium value without any applied stress. This length (r_0) is related to the number of monomers between two stickers (N) and the size of the monomer (b) by :

$$r_0^2 = C_\infty . N . b^2 \qquad (12)$$

With $N = \frac{M_S}{m_0}$ where Ms is the mass between stickers defined in section 3.1.1 and m_0 is the monomer molar mass.

The following system of equations enable to determine the critical extension ratio (λ_c) from molecular parameters :

$$\left.\begin{array}{c} \mathrm{r}_0^2 = \mathrm{C}_\infty . \mathrm{N} . \mathrm{b}^2 \\ r_0 = \sqrt{C_\infty . N} . b \\ r_{max} = N . b \end{array}\right\} \lambda_c = \frac{N}{\sqrt{C_\infty . N}} = \sqrt{\frac{N}{C_\infty}} \qquad (13)$$

Then it is possible to express the critical deformation as follows :

$$\varepsilon_c = \sqrt{\frac{N}{C_\infty}} - \frac{C_\infty}{N} \; because \; \varepsilon_c = \lambda_c - \frac{1}{{\lambda_c}^2} \qquad (14)$$

Finally, the characteristic ratio C_∞ is estimated from equation 14 which is solved taking a monomer mass (m_0) of 265 g/mol for cellulose acetate with a DS of 2,45 and a critical deformation (ε_c) between 0,4 and 0,6 according to experimental results. The mass between stickers (Ms) is considered as constant up to 35wt% of triacetin and its value is around 12000 g/mol at 180°C according to the rubber plateau modulus (G_N^0) determined by SAOS measurements.

Equation 14 gives a value of C_∞ between 30 and 34 according to the critical deformation retained. This estimation is rather close to the value of 36 found in the literature (Lapasin & Pricl, 1995). Cellulose acetate chains are highly rigid because of ~~primary and secondary~~ intramolecular hydrogen bonds within a chain (Hsieh & Kadla, 2012; Kawanishi et al., 1998). In the melt state, the presence of plasticizer seems to not have an evident effect on the presence of the intramolecular interactions because of the conservation of a similar C_∞.This result also confirms that, for plasticized cellulose acetate, elasticity stems from elastic segments between “close state” stickers which lead to strain hardening effects when solicited above a critical deformation during uniaxial extensional flow.

3.4 Large amplitude shear experiments at low plasticizer contents

For transient networks such as entanglements, strong elastic behaviour is observed under elongational flow whereas strain softening is always observed under shear flow. In order to check if this behaviour could be verified for this system, large amplitude shear experiments have been carried out for low plasticized samples. Because of experimental constraints described in section 2.3, measurements were performed with parallel-plate fixture. Therefore, the results are only qualitative and elasticity effects of plasticized cellulose acetate were then highlighted following the evolution of the normal force generated by sheared samples (Figure 8). The increase of the normal force is classically related to the Weissenberg effect appearing after a critical shear rate because of the development of a strong elasticity in the polymer. The critical shear rate for Weissenberg effect seems not really depend on plasticizer content and temperature. On the contrary, the intensity of this effect depends strongly on plasticizer content and temperature for the range of shear studied.

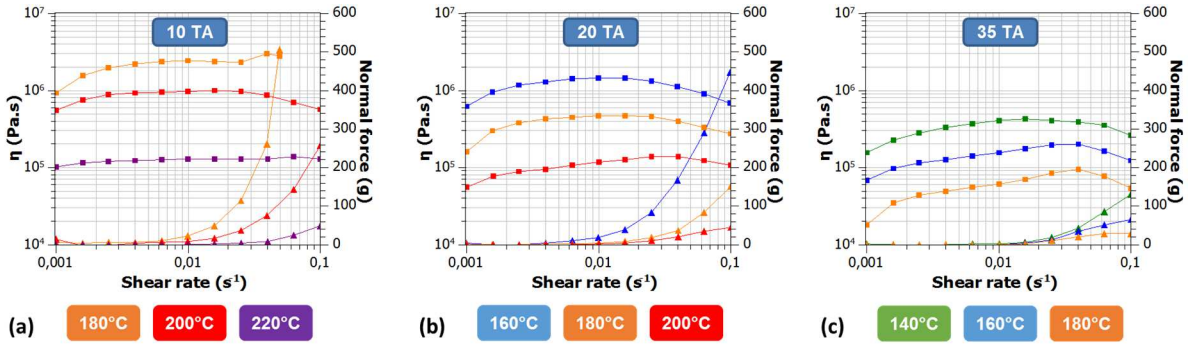


Figure 8 : Evolution of the steady-shear viscosity (■) and the normal force (▲) as a function of shear rate at different temperatures for 10 (a), 20 (b) and 35wt% (c) of triacetin.

In any case, the Weissenberg effect appeared at really low shear rates and without any noteworthy modification of the viscosity. Once again, this surprising behaviour may be related to the presence of stickers between cellulose acetate chains. According to some results in the literature concerning hydroxyl-functionalized polypropylene (PPOH) copolymers, hydrogen bonds could be responsible for the high elasticity of a polymer during shear sweeps (Gupta, Yuan, Mike Chung, Cakmak, & Weiss, 2016). If the temperature increases, the network formed by hydrogen bonds is weakened and the association time of the stickers decrease (Brassinne, Cadix, Wilson, & Ruymbeke, 2017). At the same temperature, the triacetin content also influences the association time and have an effect on the intensity of the Weissenberg effect.

However, cellulose acetate is well known to contain small amount of crystalline phase even beyond the glass transition temperature Tg that could act as crosslink points and could be responsible for the specific rheological behavior. When the degree of substitution decreases to 2,5, transitions related to crystallinity are visible but their intensity turns out to be quite low, especially for X-ray diffraction (XRD) measurements (T.G. Fawcett et al., 2013) or by mechanical analysis dynamic (DMA) (M. Scandola & G. Ceccorulli, 1985.). Several papers have shown that pure cellulose acetate (not plasticized) of degree of substitution 2.45 has a degree of crystallinity from 9 to 16% (M. Sousa et al., 2010; C. Bao, 2015) and therefore are predominantly amorphous. Moreover, crystallinity decreases for plasticized CA (M. G. A. Vieira, M. A. da Silva, L. O. dos Santos & M. M. Beppu 2011; M. Bocqué, C. Voirin, V. Lapinte, S. Caillol & J.-J. Robin, 2016 ; M. Scandola & G. Ceccorulli, 1985). Actually, the role of crystallinity on the peculiar rheological response can be ruled out because, if crystalline phase is present and acts as crosslink, plasticized CA should behave as rubber with permanent long term elasticity while terminal flow of plasticized CA is observed (Figure 1 and 4).

4. Conclusion

Thanks to the evolution of rheological parameters, it has been shown that rubber elasticity of plasticized cellulose acetate is not related to classical entanglements but rather to another correlation length corresponding to the distance between strong but labile interactions, called stickers, between cellulose acetate chains. The stickers could be related to residual hydrogen bonds between cooperative hydroxyls groups of two AGU units of neighboring cellulose acetate chains. Stickers are characterized by a finite lifetime enabling connection and reconnection leading to transient network formation. Therefore, plasticized cellulose acetate in the melt state has characteristics of associating polymers.

Up to a critical content of 35wt%, the plasticizer could be localized in the free volume defined between two consecutive stickers of neighboring cellulose acetate chains. Therefore, the plasticizer modifies the local environment of the chains at the monomer scale but there is no modification of the structure at the scale of the bulk and the rheological parameters depending on the whole chain remained unaffected. These stickers confer an unusual viscoelastic behaviour to cellulose acetate at short times and unexpected scaling behaviour regarding the different rheological parameters studied by SAOS. Moreover, if the samples are compared at the same distance to Tg, no effect of the nature of the plasticizer on the dynamics of chains is found up to 35wt%. On the timescale studied by dynamic oscillatory measurements, the global molecular dynamics are unaffected by the addition of plasticizer.

The strong interactions between cellulose acetate chains also have an effect at high deformation and confer unusual flow behaviour. A strain hardening effect, whose intensity is not dependent upon the triacetin content up to 35wt%, was noticed thanks to uniaxial extensional flow at different extensional-strain rates. Strain hardening appears at a same critical deformation for the different plasticizer content and the results fit with a Lodge model. It means that there are indeed permanent interactions on the experimental timescale. The strong elasticity of the polymer was also highlighted thanks to shear sweeps because of the apparition of a Weissenberg effect after a critical shear rate. This phenomenon appeared at really low shear rates and without any noteworthy modification of the viscosity. According to the literature, hydrogen bonds could be responsible of the high elasticity of a polymer during shear sweeps.

This work opens the way for further investigation of the structural organization of cellulose acetate chains in the melt state and more particularly the organization of the chains according to their molar mass and the study of long term relaxation.

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