Carbohydrate Polymers 116 (2015) 95–102

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

# Miscibility and dynamical properties of cellulose acetate/plasticizer systems

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ARTICLE INFO

*Article history:*
Received 17 December 2013
Received in revised form 24 June 2014
Accepted 28 July 2014
Available online 20 August 2014

*Keywords:*
Cellulose acetate
Plasticization
Thermo-mechanical properties
Dielectric relaxation
Diethyl phthalate
Miscibility

ABSTRACT

Due to its biodegradability and renewability, a great interest has been devoted to investigating cellulose acetate in order to expand its potential applications. In addition, secondary cellulose acetate (CDA) could also be considered as a model system for strongly polar polymer system. The dynamical behavior of CDA is supposed to be governed by H-bonding and dipolar interaction network. Due to their high glass transition temperature, cellulose acetate-based systems are processed when blended with plasticizers. It is thus of utmost importance to study the miscibility and plasticizing effects of various molecules. We prepared CDA films via solvent casting method with diethyl phthalate as the plasticizer. Miscibility diagrams were established by calorimetry and thermo-mechanical (DMTA) experiments. Dynamical properties were analyzed by DMTA and broadband dielectric spectroscopy. We could identify the α-relaxation of these CDA-plasticizer systems in the frequency range from 0.06 Hz to $10^6$ Hz, which allowed for describing the dynamics in the so-called Williams-Landel-Ferry/Vogel-Fulcher-Tammann regime.



## 1. Introduction

The dynamical properties of polymers are a topic of great current interest. One overall goal is to be able to predict the viscoelastic response of a given system on the basis of knowledge of its composition and the component molecular weights. Polymers with a dense network of strong polar interactions such as cellulose form a particular class of systems with specific issues (Feldmann, Kade, Meijer, Hawker, & Kramer, 2009), which is the subject of interest of this manuscript. However, due to its semi-crystalline nature, the processability of cellulose needs to be improved by acetylation process. Cellulose diacetate (CDA, with a degree of substitution of 2.45) is thus chosen as an example for representing and for studying highly polar polymer systems. CDA is prepared from cellulose via the well-known acetylation process: substitution of hydroxyl groups of cellulose by acetyl groups. The acetylation level of cellulose acetate is then defined by a special term: degree of substitution (DS). It is believed that its dynamical behavior is somehow governed by H-bonding and dipolar interaction network.

Due to its biodegradability and renewability, a great interest has been devoted to investigating cellulose and its derivatives in order to expand their potential applications. Among them, cellulose acetate (CA) has gained special attention in the past few years thanks to its potential market shares in textiles, food and pharmaceutical industries. Unfortunately, the melting temperature of cellulose acetate is close to its decomposition temperature which makes the industrial processes difficult to optimize. Thus for CA's melting processing and injection molding, one needs to use plasticizers. In this context, extensive research has been dedicated to identify efficient plasticizers (Fordyce, & Meyer, 1940).

Considerable studies have been carried out on commercial cellulose acetate (CDA) and its plasticized samples. Differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) have been largely applied to characterize these samples (Choi et al., 2005; Fringant, Rinaudo, Foray, & Bardet, 1998; Kawai and Hagura, 2012; Keely, Zhang, & McBrierty, 1995; Miyashita, Suzuki, & Nishio, 2002; Scandola and Ceccorulli, 1985a; b). An extensive investigation of thermal properties of cellulose acetate with different degrees of substitution (DS of 0.49, 1.75, 2.46, and 2.92) was published by Kamide and Saito, 1985. Dielectric relaxation spectroscopy (DRS) can be used to investigate molecular motions in a wide frequency range. DRS studies on different polysaccharides have been reported in the literature, but mainly for secondary relaxations (Einfeldt, Meibner, & Kwasniewski, 2001; Jafarpour, Dantras, Boudet, & Lacabanne, 2007; Kaminski et al., 2009; Kusumi, Teramoto, & Nishio, 2011; McBrierty, Keely, Coyle, Xu, & Vij, 1996; Roig, Dantras, Dandurand, & Lacabanne, 2011; Seymour, Weinhold, & Haynes, 1979; Sousa, Bras, Veiga, & Ferreira,

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http://dx.doi.org/10.1016/j.carbpol.2014.07.078
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2010). However, low frequency studies are difficult due to important conductivity interferences. To the best of our knowledge, no complete studies regarding the terminal α-relaxation of cellulose acetate by DRS have been published.

Most of these dielectric studies, however, have been focused on cellulose and its derivatives, and only few results have been reported about dielectric properties of plasticized cellulose acetate systems. Seymour et al., 1979 focused on phthalate plasticizers such as dioctyl phthalate and diphenyl phthalate. McBrierty et al., 1996 studied the dynamics of cellulose acetate with 26 wt% diethyl phthalate. The CDA's dielectric constant has been found to be about 4–6 (Rustemeyer, 2004), depending on the applied frequency. The dielectric constants of dibutyl phthalate (6.4) and dimethyl phthalate (8.5) have been reported (Maryott, & Smith, 1951), which should provide a lower and upper bound for that of diethyl phthalate.

The paper is organized as follows. In Section 2, we describe how we prepared CDA films via solvent casting method with diethyl phthalate (DEP) as the plasticizer. Miscibility diagrams established by calorimetry (MDSC) and thermo-mechanical experiments (DMTA) are discussed in Section 3.2. Dynamical properties (α-relaxation and secondary relaxations) are analyzed by DMTA and broadband dielectric spectroscopy (BDS) in Section 3.3 and 3.4.

## 2. Materials

Cellulose acetate sample with an average DS of 2.45 was supplied by Solvay Acetow GmbH (Freiburg, Germany). Diethyl phthalate was obtained from Sigma Aldrich (Saint Quentin Fallavier, France). Acetone was purchased from VWR International (Fontenay-sous-Bois, France). All chemicals were used as received.

### 2.1. Film preparation

CDA and diethyl phthalate mixtures in the desired weight proportions were dissolved in acetone at a concentration of 10 wt%. The solutions were stirred for at least 24 h at room temperature and then poured into a Teflon tray. Films were made by slow solvent evaporation at room temperature and stored in a desiccator until analysis. Trace amounts of water were quantified by Karl Fischer titration at 160 °C. Sample drying procedure is described in the Supplementary Information file (Table 1). We could check by Karl Fischer titration that the remaining water content never exceeded 0.5 wt% (see Table 2 in the Supplementary Information file). The plasticizer loss measured by weighing our samples did not exceed 12% of the nominal amount (see Table 3 in Supplementary Information file). The results in Table 3 can be considered as error bars regarding the DEP content of our samples. Plasticizer content was also verified by $^1$H NMR spectroscopy. Samples were prepared using acetone-$d_6$. Tetramethylsilane (TMS) was used as internal standard. $^1$H NMR spectra were measured over the range of 0–15 ppm with a Bruker 300 MHz instrument (Karlsruhe, Germany). Pyrrole was used as the reference.

### 2.2. Modulated differential scanning calorimetry (MDSC)

MDSC measurements were performed by using a Q2000 differential scanning calorimeter (TA Instruments, United States) equipped with a liquid $N_2$ cooling device (LNCS). Indium was used for temperature and heat flow calibration. Sapphire was used to calibrate the MDSC reversing heat capacity signal. For each measurement, 5–10 mg of material was sealed into a Tzero aluminum pan and placed in the autosampler. Certain samples were preconditioned at 70 °C for 15 min to eliminate any residual solvent (the loss of water could also be observed). Thermograms were recorded during heating at a scanning rate of 5 °C/min. Modulation was performed every 40 s at ± 2 °C. Glass transition temperatures were determined from the second scan in order to discard the influence of thermal history.

### 2.3. Dynamic mechanical thermal analysis (DMTA)

A Rheometrics Scientific analyzer RSA II was used to perform DMTA measurements. Samples were cut into rectangular films having the following dimensions: length of 26.5 mm, width of 4.5 mm, and thickness of 0.3 mm. Strain limit was fixed at 0.02%. Curves were recorded at a fixed frequency 1 Hz during heating from −100 °C at a scanning rate of 2 °C/min. Relaxation temperatures were determined from the peak of tan $\delta$ plot.

### 2.4. Dielectric relaxation spectroscopy (DRS)

DRS measurements were carried out in the frequency range of 0.06–$10^7$ Hz by means of an Alpha-N analyzer from Novocontrol GmbH (Hundsangen, Germany). Isothermal frequency scans were performed from −130 °C up to 200 °C in steps of 4 °C/scan. Temperature was controlled to better than 0.1 °C with a Novocontrol Quatro cryosystem. Parallel gold-plated electrodes with a diameter of 20 mm were used. The sample thickness was 0.3–0.4 mm.

### 2.5. X-Ray Diffraction (XRD)

X-ray diffractograms were measured on a Bruker D8 Advance diffractometer (Bruker, Germany) by refraction method using nickel-filtered CuKα radiation (λ = 1.5406 Å) operated in the $\omega$-2$\theta$ scanning mode between 1 and 90° (2$\theta$).

## 3. Results and discussions

### 3.1. Thermal properties

The thermal properties of the unplasticized cellulose acetate (DS = 2.45) film are investigated by Modulated DSC. The respective thermogram is consistent with those published in the literature (Keely et al., 1995; Rustemeyer, 2004). In a first stage, glass transition temperature ($T_g$) of CDA sample is found to be close to 192 °C in the reversing heat flow, which is consistent with the temperature (200 °C) found by Kamide and Saito, 1985.

Several small endothermic peaks in the non-reversing heat flow (from 150 to 250 °C) have been identified as melting processes. In the book chapter by Zugenmaier, 2004 (in Rustemeyer, 2004) the authors mentioned other observations of two or sometimes even more endothermic peaks in CDA samples as reported in the literature. This wide distribution could be explained by the fact that there are many heterogeneous micro-crystalline systems present in the sample, which are supposed to be composed of cellulose triacetate (CTA) blocks. Note that among cellulose and its acetylated derivatives, only cellulose itself and cellulose triacetate crystallize.

For CDA samples, it is difficult to accurately determine the melting enthalpy due to the broadness and low intensity of the melting peaks, which is thought (Rustemeyer, 2004) to result from the wide distribution of crystallite sizes. We estimate the melting enthalpy to be 9.8 J/g at 240 °C, from which we obtain a degree of crystallinity of 16.7%. During the second heating run, the melting enthalpy has decreased down to 5.1 J/g (degree of crystallinity ≈9%). Note that the CDA's degree of crystallinity is estimated with $\Delta H^0_m = 58.8$ J/g proposed by Cerqueira, Filho, & Assuncao, 2006. At higher temperatures, the sample undergoes decomposition (data not shown).

X-ray Diffraction (XRD) is applied in order to study the crystallinity of unplasticized CDA film prepared via solvent casting method. The obtained diffractograms are consistent with those

given by the International Centre for Diffraction Data (ICDD) database: PDF $n^{\circ}$ 00-062-1713 (Fawcett et al., 2013). Three crystalline peaks are identified in a mainly amorphous background signal. Those peaks are not intense which confirms a low degree of crystallinity of the unplasticized CDA film sample. These results are also consistent with those obtained by Boy, Schulken, & Tamblyn, 1967; Scandola and Ceccorulli, 1985a; Sousa et al., 2010 who reported a low degree of crystallinity.

### 3.2. Miscibility behavior of secondary cellulose acetate plasticized by diethyl phthalate

One needs first to characterize the miscibility range of cellulose acetate/plasticizer blend. We do it by measuring the glass transition temperature of the blend, either by calorimetry (MDSC), or by thermo-mechanical spectroscopy (DMTA). The glass transition is identified either by a jump of heat capacity (MDSC) or by a peak in tan $\delta$ (DMTA). When only one $T_g$ is present, we assume that the blend is miscible. On the other hand, when two glass transitions are present, we conclude that the blend is not totally miscible at the chosen CDA/DEP composition, with a plasticizer-rich phase and a CDA-rich phase. This analysis is made possible because both constituents have very different $T_g$s. In the crossover between these two regimes, a broadening of the glass transition is observed.

We observe that the plasticized CDA films are transparent to the naked eye. However, it should be noted that the refractive index of the two materials appear to be quite close to each other (1.502 for DEP and ca. 1.47–1.48 for cellulose acetate with DS > 2). A thermal transition of pure DEP has been found at −88 °C by MDSC technique with LNCS cooling system. A similar result (−87.3 °C) has been reported by McBrierty et al., 1996. Scandola and Ceccorulli, 1985b determined the $T_\alpha$ of DEP at −63 °C by DMTA measurements at frequency 3 Hz. The behavior of α-relaxation of DEP in dielectric spectroscopy is well described by Pawlus, Paluch, Sekula, Ngai, Rzoska, & Ziolo, 2003. We observed that the glass to rubber transition of cellulose diacetate is shifted to lower temperatures with increasing amounts of DEP. Note that the loss of DEP molecules could be detected from 100 °C (see "Supplementary Information" file). Therefore, a macromolecular plasticizer would be more advantageous.

A single glass transition has been found for CDA films containing less than 25 wt% of DEP. Two different glass transition regions have been identified for films containing more than 25 wt% of DEP. All measured $T_g$ values are composition-dependent and lay in the temperature range between those of the individual pure components. This indicates that phase separation occurs above 25 wt% of DEP content.

The $T_g$s could not be fitted by the Fox equation (Fox, 1956) given by:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}, \quad (1)$$

where

- $T_{g1}$ is the glass transition temperature of the pure polymer
- $T_{g2}$ that of plasticizer
- $w_1$ and $w_2$ the weight fraction of each component

Indeed, deviations are observed (see Fig. 1). This could be explained by the fact that the Fox equation is an empirical model for polymer-diluent system without taking into account specific interactions such as hydrogen bonds, which predominate in CDA/DEP system.

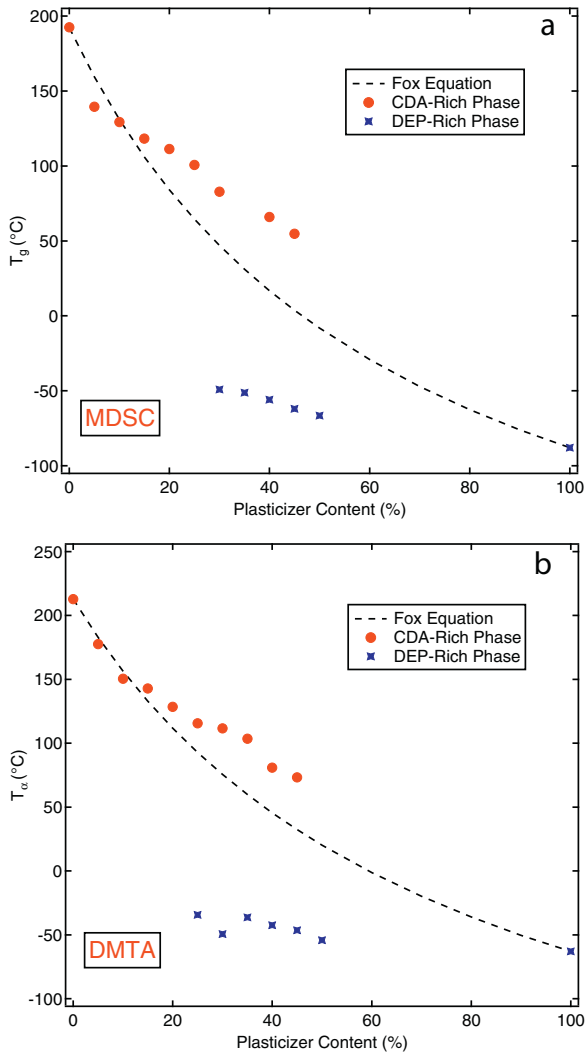


**Fig. 1.** Glass transition temperatures of CDA/DEP systems, as functions of DEP content. Dashed lines represent the $T_g$ given by Fox equation assuming miscibility. Red points: experimental $T_g$ of CDA-rich phase. Blue points: experimental $T_g$ of DEP-rich phase.

### 3.3. Thermo-mechanical properties

In Fig. 2, we plotted the Young's modulus $E'$ and tan $\delta$ measured at frequency 1 Hz, as functions of temperature for unplasticized and plasticized CDA systems with different DEP contents. The different tan $\delta$ peaks that we observe are denoted α, $\beta^*$ (shoulder) and β (from higher to lower temperatures).

The α-relaxation corresponds to the onset of segmental motion and occurs at 212 °C for the unplasticized CDA sample, which is consistent with MDSC results. When increasing the DEP content, the α-relaxation shifts to lower temperatures due to the plasticization effect of DEP, as shown in Fig. 2. We interpret the $\beta^*$ shoulder as being due to relaxation of water molecules. Note that the presence of this peak is concomitant to the loss of water when heating the samples.

Regarding β-relaxation, different views are present in the literature (McBrierty et al., 1996; Seymour et al., 1979; Scandola and Ceccorulli, 1985a). The interpretation of the secondary β-relaxation of unplasticized CDA system is still disputed. It could either be due to the motion of single monomeric unit or corresponding to a cooperative motion involving side groups and cellulosic main chain.

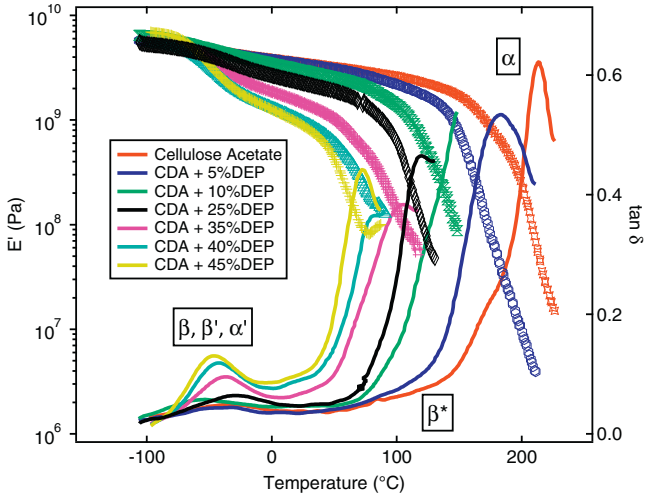


**Fig. 2.** Storage modulus and damping factor tan $\delta$ obtained by DMTA investigation. We indicated the occurrence of different relaxation processes in the figure. See text for more details.

In the plasticized CDA system, only one broad relaxation peak has been observed around −50 °C. However, we assume that the observed peak results from two different contributions: β-relaxation of unplasticized CDA and β'-relaxation of plasticized CDA. The β'-relaxation is specific to the CDA/DEP system and has a different molecular origin than that of the β-relaxation. The hypothesis is based on the fact that the characteristic temperatures of the secondary relaxation peak are not the same for all systems. As CDA requires certain amounts of DEP molecules to be completely plasticized, both β- and β'-relaxations exist in the plasticized CDA samples until the immiscibility threshold. Upon increasing plasticizer content, the proportions of these two contributions change. Upon further increasing DEP content, we assume that phase separation takes place. Indeed, the observed peak is shifted to lower temperatures, and its magnitude is increased with increasing DEP content. This temperature shift is quite similar as the shift of $T_g$ of DEP-rich phase in MDSC result. MDSC is only sensitive to primary relaxation phenomenon. Thus, we assume that the observed peak results from contributions of β'-relaxation of plasticized CDA and α'-relaxation of DEP-rich phase, which is consistent with an assumed partial miscibility of the CDA/DEP systems. Note that this interpretation, as well as a precise description of the involved molecular motions will require further studies.

In the literature, Seymour et al., 1979 focused on various cellulose ester/plasticizer systems studied by DMTA and dielectric measurements. They argued that the secondary relaxation of polymer-plasticizer systems is due to a specific type of polymer–plasticizer interaction, which is denoted as "β' relaxation". The CDA-DEP system has also been studied by Scandola and Ceccorulli, 1985b, but mainly with DMTA analysis. With similar experimental results, the Italian group suggested "an active participation of the diluent molecules in the motion responsible for the secondary relaxation at high DEP contents". On the other hand, they assumed miscibility at DEP contents lower than 50 wt%.

### 3.4. Dielectric study

In order to minimize the loss of plasticizer, samples are dried in the vacuum of dielectric instrument at specified temperatures (see Table 1 in the Supplementary Information file). This drying process also improves the contact between the sample and the electrodes, so that the recorded signals are more reliable. Due to DEP toxicity issues, we restricted the temperature range depending on the DEP content.

**Table 1**
Activation energies and pre-exponential factors for the secondary relaxations of cellulose diacetate + DEP samples obtained from the results in Fig. 5.

| | γ Relaxation | | β Relaxation | |
|---|---|---|---|---|
| Sample | Log $\tau_0$ | $E_a$ (kJ/mol) | Log $\tau_0$ | $E_a$ (kJ/mol) |
| Dried Cellulose Diacetate | −16.3 | 50 | −18.6 | 78 |
| CDA + 15% DEP | −15.9 | 47 | −22.0 | 92 |
| CDA + 25% DEP | N/A | N/A | −23.6 | 95 |
| CDA + 35% DEP | N/A | N/A | −29.4 | 120 |
| CDA + 45% DEP | N/A | N/A | −32.9 | 130 |

The commercial software "WinFit" was used to fit the isothermal dielectric relaxation data by using a sum of the model function introduced by Havriliak and Negami (Havriliak and Negami, 1967):

$$\varepsilon*(\omega) = \varepsilon_\infty + \Sigma j \frac{\Delta\varepsilon_j}{\left[1+(i\omega\tau_j)^{\alpha_{HNj}}\right]^{\beta_{HNj}}}, \quad (2)$$

where

- $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ is the dielectric strength (the difference between the real permittivity values at the low and high frequency limits)
- $\tau \approx (2\pi f_{max})^{-1}$ is the characteristic relaxation time
- $\alpha_{HN}$ and $\beta_{HN}$ are the shape parameters ($0 < \alpha_{HN} < 1$, $0 < \alpha_{HN}.\beta_{HN} < 1$)
- $j$ is the number of relaxation processes

For secondary relaxations, $\beta_{HN}$ is fixed equal to 1, as commonly acknowledged in the literature (Cole and Cole, 1941; 1942). On the other hand, α-relaxation of the plasticized system could be identified but needs to be analyzed with isochronal dielectric relaxation data due to the experimental limitations.

First consider the results for the unplasticized CDA film (DS = 2.45, with less than 0.5 wt% water), for which a 3D plot of imaginary part of permittivity vs. frequency and temperature is shown in Fig. 3a. A close inspection of the obtained spectra reveals that two secondary relaxation processes are detected (named β and γ relaxations). Note that only one secondary relaxation is identified on totally dried cellulose acetate samples in the literature (Sousa et al., 2010). We interpret the presence of two peaks in our results as the consequence of the presence of water traces in our samples. The potential influence of water on the dielectric properties of CDA film is calculated with its dielectric constant. 0.5 wt% is the most significant amount of water that we could find in all dielectric samples. The dielectric constant of water at ambient temperature is about 80. 0.5 wt% * 80 = 0.4, this should be the biggest water contribution to the real part of complex permittivity. This contribution is negligible compared to the contribution of cellulose acetate whose dielectric constant is about 4–5.5 in the high frequency conditions.

Cellulose acetate (DS = 2.45) has a very high glass transition temperature and its melting temperature is very close to its degradation temperature. Furthermore, in the high temperature regime where one could observe α-relaxation, conductivity takes place which is another limitation on dielectric measurements. This is probably the reason why α-relaxation of cellulose acetate has never been thoroughly studied with dielectric spectroscopy.

The 3D plot of permittivity" vs. frequency and temperature for cellulose diacetate/diethyl phthalate (35 wt%) system is shown in Fig. 3b. The following secondary and primary relaxations are identified:

- γ' Relaxation (the third and fastest secondary relaxation process)
- γ Relaxation (faster secondary relaxation process)
- β' Relaxation (slower secondary relaxation process)

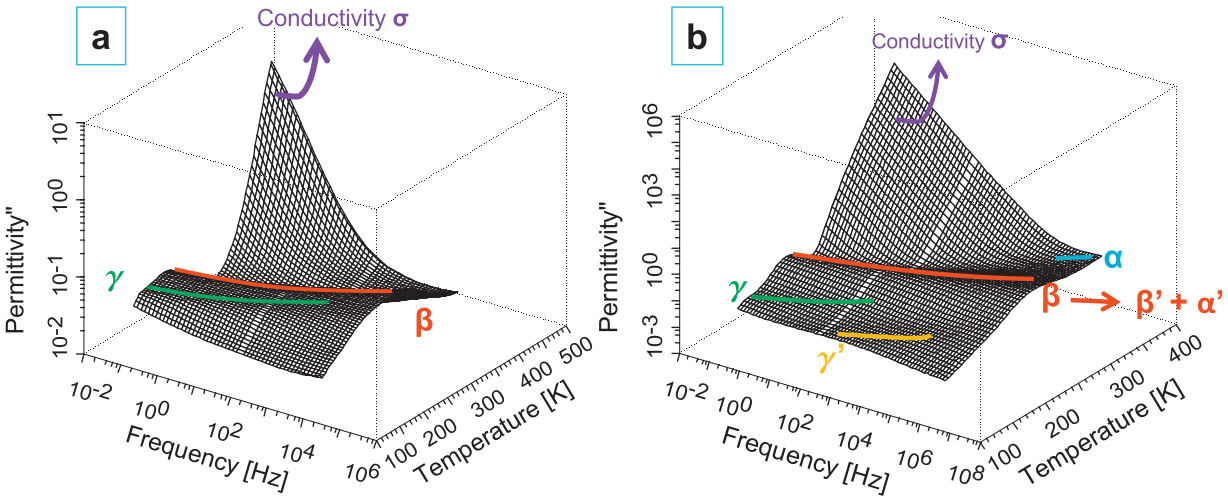


**Fig. 3.** a. 3D plot of the dielectric loss for unplasticized cellulose diacetate. b. 3D plot of the dielectric loss for CDA + 35% DEP. We indicate in the figure the position of various relaxation processes. We also observe the conductivity peak at low frequency/high temperature domain.

- α' Relaxation (final relaxation of the DEP-rich phase above the phase separation threshold)
- α Relaxation (final relaxation of the CDA-rich phase)

The imaginary part of the complex dielectric permittivity is plotted as a function of frequency in Fig. 4, for various plasticizer contents. The measurements have been performed at temperature −90 °C (Fig. 4a) and at −40 °C (Fig. 4b).

In Fig. 4a we plotted the dielectric response of unplasticized CDA, normalized by a factor 0.8, in order to quantitatively compare the results with the dielectric response of the CDA + 15% DEP sample. Note that the γ'-relaxation is clearly absent for the unplasticized CDA. We deduce then that this relaxation does not correspond to water molecules' motions but is attributed to DEP molecules, or to localized molecular motions of the DEP-plasticized CDA. Discriminating between these two possibilities and describing in detail this relaxation mechanism will require further studies.

At T = −40 °C we observe in Fig. 4b a broad peak. Our point of view is that this peak corresponds to the three different relaxation processes which we denoted β, β' and α' above (see discussion regarding Fig. 3b, and Fig. 2 for mechanical results). The observed peak corresponds to the superposition of at least two relaxations: β- and β'-relaxations below the immiscibility threshold and β'- and α'-relaxations above the phase separation threshold.

The temperature dependence of the relaxation rate of secondary relaxations can be described in general by an Arrhenius law:

$$\tau(T) = \tau_0 \exp\left(\frac{E_a}{k_B T}\right), \quad (3)$$

where $E_a$ the activation energy, $\tau_0$ the characteristic time and $k_B$ is the Boltzmann's constant (Kramers, 1940).

Fig. 5 illustrates the so-obtained temperature dependence behavior of secondary relaxations. It is until now impossible to separate the β-, β'- and α'-relaxations from each other. Thus for following activation energy calculations and so on, we denote "β-relaxation" (as in Fig. 5 and Table 1) to represent the broad dielectric peak contributed from these 3 relaxation processes.

In the unplasticized system, it is found that the β- and γ-relaxations are well described by the Arrhenius law. From the slope of the curves in Fig. 5, we find $E_a$ = 78 kJ/mol for the β-relaxation and $E_a$ = 50 kJ/mol for the γ-relaxation. By gathering results from the literature, Sousa et al., 2010 proposed that the activation energy of the γ-relaxation is bounded between 32 and 52 kJ/mol, which is confirmed by our data. Note that the value of the characteristic time $\tau_0$ is consistent with previous estimates. Regarding the activation energy of the β-relaxation, the same authors provided a range between 76 and 85 kJ/mol, which is also confirmed by our data. Regarding the plasticized systems, we can observe that both γ-relaxation process and β-relaxation process at low DEP content (below the immiscibility threshold) obey approximately the Arrhenius law. Moreover, the γ-relaxation of the plasticized system (e.g. CDA + 15% DEP) is described by almost the same parameters as those of the unplasticized CDA, from which we deduce that their microscopic mechanisms are the same. Therefore, the corresponding motion is likely to be specific to the CDA itself. On the other hand, the activation energy of the β-relaxation in the CDA/DEP system increases with increasing plasticizer content, whereas the pre-exponential factor $\tau_0$ becomes smaller and smaller. This is an indication that the corresponding process involves cooperative motions, analogous to α-relaxation (Eyring, 1936; Starkweather, 1988). Indeed, a relaxation motion with a well-defined energy barrier should have at least a characteristic time of order of $10^{-13}$ s. The same interpretation has been proposed by several other authors (Montès, Mazeau, & Cavaillé, 1997; Kaminski et al., 2009).

### 3.4.1. *Phase separation effect on dielectric relaxations*

Above 25% of DEP, the dielectric strength of the β'-relaxation increases dramatically (Fig. 4b) and its relaxation time shifts slowly to that of the primary relaxation of pure plasticizer. Our interpretation is that the observed dielectric peak is the superposition of the β'-relaxation of the plasticized CDA and of the α'-relaxation of the DEP-rich phase. It is thus strongly observed above the immiscibility threshold. The relaxation time distributions of these two relaxation processes are too close to be separated.

We propose to attribute the α'-relaxation to the final relaxation of the DEP-rich phase. This point of view is consistent with the mechanical results, for which we observe two relaxations e.g., for the CDA + 45% DEP sample (Fig. 2). Indeed, we assume that the relaxation at −50 °C corresponds to the final relaxation of the DEP-rich phase, whereas the final relaxation at 80 °C corresponds to the final relaxation of the CDA-rich phase. No other relaxation is observed in Fig. 2, in particular which would correspond to specific DEP molecular motions.

At DEP content larger than 25%, we can see from Fig. 5 that the temperature dependence of β-relaxation times cannot be

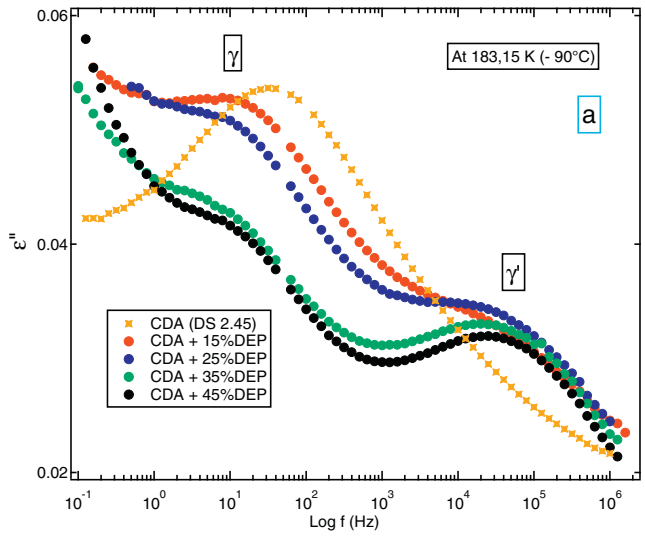


**Fig. 4.** a. Frequency dependence of the imaginary part of the complex dielectric permittivity ($\varepsilon$") at 183.15 K (−90 °C), for cellulose diacetate/diethyl phthalate systems. We indicate in the figure the position of two different secondary relaxation processes. b. Frequency dependence of the imaginary part of the complex dielectric permittivity ($\varepsilon$") at 233.15 K (−40 °C), for cellulose diacetate/diethyl phthalate system. Several relaxation processes are superposed (see text for more details).

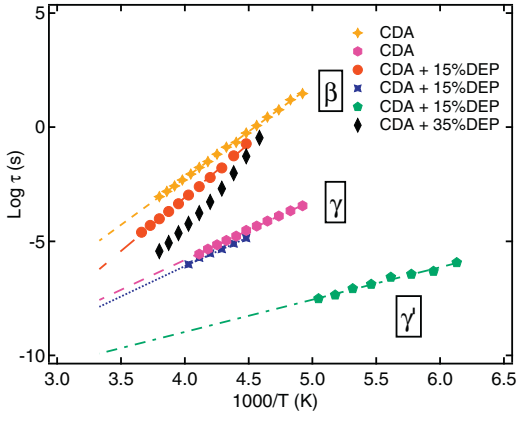


**Fig. 5.** Temperature dependence of relaxation times ($\tau$) for 3 relaxation processes detected in the unplasticized and plasticized cellulose diacetate. β-relaxation here contains contributions of all possible relaxation processes (β, β' and α') in this temperature/frequency range.

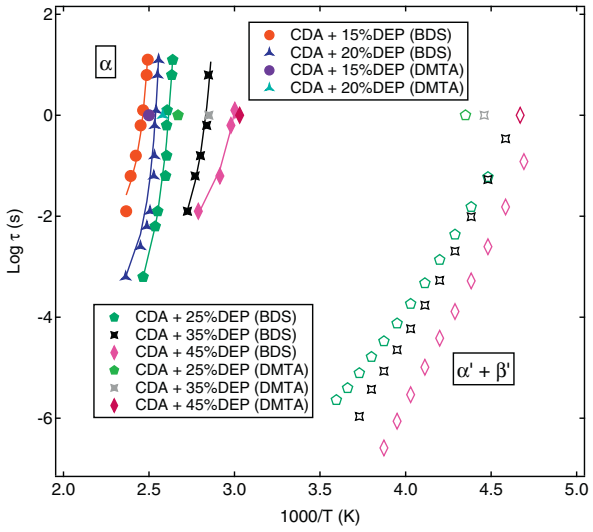


**Fig. 6.** Temperature dependence of α-relaxation times ($\tau$) in cellulose diacetate/DEP systems. Data obtained by mechanical and dielectric measurements.

described by an Arrhenius law but a Vogel-Fulcher-Tammann (VFT) law (Vogel, 1921; Fulcher, 1925; Tammann and Hesse, 1926):

$$k = Ae^{-DT_0/(T-T_0)}, \quad (4)$$

where D is a dimensionless constant and $T_0$ denotes the so-called Vogel temperature. Note that VFT law is usually used to describe the temperature dependence of primary relaxation times. The deviations from Arrhenius law are larger at higher DEP content (see Table 1). This is an additional indication that the β'-relaxation is superposed with α'-relaxation of DEP-rich phase.

### 3.4.2. *Interpretation of α relaxation*

As previously mentioned, it is difficult to study the primary relaxation of unplasticized cellulose acetate system due to thermal degradation. However, plasticized cellulose acetates, such as CDA/DEP systems have a lower glass transition temperature which may allow studying the α-relaxation process by dielectric spectroscopy in a large frequency range.

Please note that the characteristic dielectric relaxation time is obtained with complex permittivity plot against temperature, which has relatively large error bars. The mechanical relaxation time is determined with the *E*" plot against temperature at frequency 1 Hz, in order to have equivalence with the complex permittivity. Taking into account all error margins we have, we assume that the obtained mechanical and dielectric results at log $\tau = 0$ are equivalent.

In Fig. 6 we plotted the temperature dependence of the α-relaxation times of plasticized CDA systems. At DEP concentrations smaller than the partial miscibility limit, a single α-relaxation is observed. At higher concentrations, one observes two α-relaxation processes associated to the CDA-rich and DEP-rich phases, respectively. The experimental curves are fitted with the VFT equation (4). The corresponding parameters are given in Table 2. We do observe indeed that the plasticizer accelerates the dynamics of cellulose acetate.

α-relaxations of plasticized CDA samples at frequency 1 Hz obtained by mechanical experiments have been added in Fig. 6 in order to compare with the dielectric results. A perfect match is obtained regarding both techniques. Our results obtained in dielectric spectroscopy (see also Fig. 1 in Supplementary Information file) do indeed correspond to the final α-relaxation of our cellulose acetate systems.

**Table 2**
Vogel temperatures and glass transition temperatures $T_g$ obtained by DSC and DMTA, for different DEP-CDA systems. DMTA temperatures are based on the $E''$ plot at frequency 1 Hz.

| | Estimated $T_0$ (K) | $T_g$ DSC (K) | $T_\alpha$ DMTA (K) |
|---|---|---|---|
| CDA + 15% DEP | 367–389 | 391 | 393 |
| CDA + 20% DEP | 379–384 | 384 | 383 |
| CDA + 25% DEP (CDA-Rich Phase) | 335–361 | 374 | 374 |
| CDA + 35% DEP (CDA-Rich Phase) | 330–344 | 348 | 351 |
| CDA + 45% DEP (CDA-Rich Phase) | 295–316 | 328 | 330 |

The mechanical α'-relaxation of CDA + 25, 35, and 45% DEP at frequency 1 Hz have also been plotted in Fig. 6. A temperature shift (10–15 °C, typically) as compared to the dielectric results is observed. However, the relaxation spectrum is very broad and these results may be considered as consistent. In particular, it is possible to explain these differences by the fact that this peak corresponds to two relaxations (β'-relaxation of plasticized cellulose acetate and α'-relaxation of DEP-rich phase), the respective amplitudes of which depend on the considered technique.

## 4. Conclusions

The dynamical properties of unplasticized and plasticized cellulose acetate (DS = 2.45) have been investigated by modulated differential scanning calorimetry, dynamical mechanical thermal analysis and broadband dielectric spectroscopy. The plasticizing effect of diethyl phthalate on cellulose diacetate has been quantified by a decrease of the glass transition temperature, as a function of plasticizer content, and also by studying the dynamics of the systems by different spectroscopy techniques. Phase separation occurs at DEP contents larger than 25 wt%. Secondary relaxations in CDA/DEP systems have been identified as γ', γ, β and β' relaxations. To the best of our knowledge, the γ'-relaxation had never been observed in the literature. Note that β and γ relaxations had already been thoroughly discussed in the literature. At plasticizer contents above the miscibility limit, we observed that the β' relaxation no longer obeys the Arrhenius law, but follows a VFT behavior. We interpreted this result as a consequence of a superposition of the α'-relaxation of the plasticizer-rich phase and of the β'-relaxation of the plasticized CDA.

The primary α-relaxation process could also be identified in DEP-plasticized CDA systems by dielectric spectroscopy. It allowed us to calculate the corresponding VFT parameters. To the best of our knowledge, such an observation had never been reported in the literature. However, more investigations will be required for studying in more details the different relaxation processes. A detailed understanding of the mechanisms regarding miscibility and phase separation in these strongly H-bonded systems still needs to be developed. This aim will require both theoretical modeling and experimental studies, e.g., of phase separation studies by Small-Angle Neutron Scattering. More refined chemical structure characterizations, e.g., by Wide-Angle Neutron Scattering and numerical modeling will be required also for a more detailed description of these systems.

## Acknowledgement

The authors thank Solvay Acetow GmbH for their kind supply of commercial cellulose acetate samples.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.07.078.

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