



Miscibility and dynamical properties of cellulose acetate/plasticizer systems



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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.

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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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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 ^1H NMR spectroscopy. Samples were prepared using acetone- d_6 . Tetramethylsilane (TMS) was used as internal standard. ^1H 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 reflection method using nickel-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5406$ Å) operated in the ω - 2θ scanning mode between 1 and 90° (2θ).

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 $\approx 9\%$). Note that the CDA's degree of crystallinity is estimated with $\Delta H_m^0 = 58.8$ 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

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