Polymer 71 (2015) 102–112

Contents lists available at ScienceDirect

Polymer

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

Rheo-optical characterization of liquid crystalline acetoxypropylcellulose melt undergoing large shear flow and relaxation after flow cessation

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ARTICLE INFO

Article history:
Received 22 April 2015
Received in revised form
26 June 2015
Accepted 30 June 2015
Available online 6 July 2015

Keywords:
Rheo-optics
Cellulose derivative
Liquid-crystal
Extrusion

ABSTRACT

The rheological and structural characteristics of acetoxypropylcellulose (APC) nematic melt are studied at shear rates ranging from 10 s^{-1} to 1000 s^{-1} which are relevant to extrusion based processes. APC shows a monotonic shear thinning behavior over the range of shear rates tested. The negative extrudate-swell shows a minimum when a critical shear rate $\dot{\gamma}_c$ is reached. For shear rates smaller than $\dot{\gamma}_c$, the flow-induced texture consists of two set of bands aligned parallel and normal to the flow direction. At shear rates larger than $\dot{\gamma}_c$, the flow induced texture is reminiscent of a 2 fluids structure. Close to the shearing walls, domains elongated along the flow direction and stacked along the vorticity are imaged with POM, whereas SALS patterns indicate that the bulk of the sheared APC is made of elliptical domains oriented along the vorticity. No full nematic alignment is achieved at the largest shear rate tested. Below $\dot{\gamma}_c$, the stress relaxation is described by a stretched exponential. Above $\dot{\gamma}_c$, the stress relaxation is described by a fast and a slow process. The latter coincides with the growth of normal bands thicknesses, as the APC texture after flow cessation consists of two types of bands with parallel and normal orientations relative to the flow direction. Both bands thicknesses do not depend on the applied shear rate, in contrast to their orientation.

1. Introduction

The most abundant polymer in nature is cellulose, as main constituent of plant cells. It presents a linear structure of β-D-glucopyranose monomers, in which free primary and secondary hydroxyl groups can be fully or partially substituted through esterification or etherification, among other chemical reactions, conferring different chemical configurations to the molecules of the cellulose derivatives [1–3]. The introduction of substituent's groups in the main chain can originate dramatic changes in the chemical and physical properties of cellulose. In particular, cellulose may become soluble in water, or in other solvents, due to the breaking of crystalline chain parts that arises from the inter- and intra-hydrogen bonding among hydroxyl groups. Furthermore, due to the presence of chiral centers in the molecules, the cellulose esters may present a cholesteric liquid crystalline phase, as a lyotropic or as a thermotropic system. When subject to shear, thermotropic cholesteric cellulose esters can present a complex viscoelastic behavior, showing rich anisotropic mechanical properties, as described by Onogi and Asada [4] for liquid crystalline polymers (LCP). These systems may undergo a cholesteric-nematic transition under shear [5] and present generally remarkable optical characteristics [6].

One of the most known cellulose derivatives that can generate liquid crystalline phases is hydroxypropylcellulose (HPC). The thermotropic phase can be observed for a certain molecular weight range in a very narrow temperature window. HPC esterification can induce the temperature scope to increase, starting from below

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http://dx.doi.org/10.1016/j.polymer.2015.06.056
0032-3861/

room temperature up to T = 180 °C, depending on polymer molecular weight and cellulose derivative. The processing of HPC into fibers and films with attractive properties, ranging from energy generation [7] to smart windows [8], essentially relied on wet techniques where HPC as well as HPC esters solutions are first formulated and then processed through knife coating or electrospinning [9]. The smart properties of the resulting cellulose derivatives products stem from changes in the orientational order of the nematic phase, achieved by variation of different external parameters, for example, temperature and UV irradiation [2], as well presence of solvent vapors [7]. Such structural changes give rise to stresses, which result in strains and modifications in film or fiber shape. Evidently, the films or fibers response to external stimuli depends on the liquid crystalline order induced during processing of the material into the final product. As such, the study of the interplay between process parameters and final structural characteristics is central to the design of the smart response to external stimuli.

The effect of shear flow on cellulose derivatives liquid crystalline thermotropic structures was reported a decade ago for acetoxypropylcellulose (APC) [10–12]. Cidade et al. [10], studied APC rheology with a rotational rheometer and explained the complex flow curve by means of a dedicated theory [13]. The flow curve exhibits three regimes. At low shear rates, the nematic polydomain texture is rearranged and partially annealed by the flow: defects break and align along the flow resulting in an almost monodomain texture and a shear thinning behavior is observed. In this flow regime, rheo-optical experiments carried out with a rotational shearing system [11] conveyed slightly different structural information: nematic domains are elongated along the flow direction and dark defects not aligned with the flow appear in polarized optical microscopy (POM). The corresponding small angle light scattering (SALS) patterns show four lobes [11]. At larger shear rates, flow affects the orientational order of APC chains in the monodomain, which is related with a quasi-Newtonian plateau located between 0.2 and 1 s^{-1} [10]. For shear rates in excess of 1 s^{-1}, shear viscosity recaptures a shear thinning behavior, whereas the first normal stress difference, N_1, exhibits an inflexion point in the otherwise monotonic increase with shear rate [10]. Depolarized SALS patterns and POM images captured in this flow regime show a streak aligned along the vorticity direction superimposed on the four lobes. The streak was assigned to striations along the flow and the increased orientation of defects in the vorticity direction was attributed to the opening of the four lobes [11].

After cessation of flow, both studies carried out on thermotropic APC [11,12] reported the formation of a stable band texture that remains during a long period. Band wavelengths with 6–8 μm were observed for a APC sample with molecular mass of 88,000 g/mol [11] and with approximately 2 μm for APC with different molecular masses (52,000 and 62,000 g/mol) [12]. In the latter, this band texture was considered as a "slow band texture", since bands remained observable after 1800 s. The authors also reported a "fast band texture" with wavelength of approximately 10 μm that appears quickly after cessation of shear and then disappears in less than 100 s, depending on temperature [12]. However, these band textures were observed after cessation of shear flows where small shear rate values were imposed (<20 s^{-1}). Furthermore, these structural phenomena have been studied by optical measurements coupled to a rotational shearing system, no *in-situ* measurement of rheological functions having been reported. An important question arises, still without a consistent answer, which deals with the sample behavior at higher shear rates. This shear rate regime is relevant for industrial polymer processes such as extrusion or melt spinning.

The rheological characterization at large shear rates (typically above 100 s^{-1}) of commercial LCPs has been widely documented in the literature. For instance, capillary rheometry showed a shear thinning behavior from 100 to 4096 s^{-1} [14]. Shear thinning was confirmed with slit rheometry, which also showed a non-linear pressure profile along the length of the slit [15] associated with the pressure dependence of viscosity of a commercial nematic LCP. LCPs are known to exhibit very low or negative extrudate swell [16], but its origin is still a matter of debate partly due to the lack of *in-situ* structural characterization, which could confirm either a strain-induced local disorientation of the nematic, or a pressure effect [15]. In this respect, the tumbling (associated with a negative first normal stress difference) or aligning behavior of thermotropic LCP in the high shear regime (regime III) is still an unresolved issue [17,18], and additional experimental data collected with LCP possessing different chain flexibility and chemical structures are still highly needed [19]. On the other hand, the structural characterization of extrudates of commercial LCPs consistently reported a band texture showing up between cross polarizers (see for instance [20] and references therein), but no information is available about band texture formation following the cessation of such fast flows. Indeed, the mechanism of band texture formation after flow cessation is not yet understood, in spite of its high industrial relevance in the fiber industry [21]. Thus, additional experimental data relating the texture time evolution with the material rheology and extrudate characteristics are highly needed to trigger new models.

In this work, we explore the high shear rate regime (regime III) of a thermotropic LCP. We aim at questioning unresolved issues associated with this regime such as: the shear-induced alignment or tumbling of nematic domains, the transition in the sign of the first normal stress difference, the formation and time evolution of band texture after flow cessation and its impact on the ultimate extrudate properties. For this purpose, we characterize, for the first time, the rheo-optical behavior of APC over a wide range of shear rates, using a rheo-optical slit die coupled to a capillary rheometer, thus extending previous efforts [10–12] to larger shear rates. Capillary rheometers equipped with slit dies are the instruments of choice to generate fast flows with polymer melts without possible experimental pitfalls associated with free surface defects (fracture), and to collect rheological data at large shear rates which cannot be achieved with rotational rheometers. Differences in shearing geometries used in previous studies [10–12,14,15,17–19] to generate flow for rheological or optical characterizations are avoided, since the rheological slit die used here allows for the *in-situ* collection of SALS patterns and POM images recorded during steady shear and after flow cessation. In addition, this experimental set-up mimics the extrusion process and allows collecting quenched extrudates at the exit of the die for ex-situ characterization. This unique combination of slit die rheometry with SALS and POM contributes to a better understanding of the rich viscoelastic behavior of APC at flow rates matching the ones found in melt processes such as extrusion. This extensive experimental study documents for the first time the relationships between flow-induced structures, melt rheological characteristics and extrudate properties in a thermotropic LCP.

2. Experimental

2.1. APC synthesis

100 g of (hydroxypropyl)cellulose (HPC) (nominal Mw = 100,000, molar substitution = 3.5 determined by ^{1}H NMR) were added to a three-neck reactor with mechanical stirring and 300 mL of glacial acetic anhydride. Subsequently, 27.5 mL of acetic acid and a catalyst for nucleophilic and esterification reactions were added to the resulting solution. The reactor was heated during eight days and