# THE VISCOELASTIC BEHAVIOR OF PITCHES

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## Introduction

The aim of this work was to investigate the viscoelastic properties of a large variety of pitches (i.e., isotropic coal-tar pitches as well as petroleum-based and synthetic mesophase pitches) in order to understand, predict, and ultimately control their complex flow behavior. Novel transient techniques were developed to help quantify the elasticity of isotropic and mesophase pitches. Also, for the first time, a predictive model was proposed that captured the development of domain structure during the flow of mesophase pitches. The following sections briefly summarize the results obtained during this study.

## Viscoelasticity of Pitches

The viscoelastic changes induced by air-blowing or heat-soaking a pitch for different periods of time were evaluated and related to the complex chemical structures created during these treatments.

*Air-Blown Pitches.* The results of the chemical characterization of a series of pitches that had been air-blown for various periods of time suggested that during air blowing aromatization initially occured, accompanied by the removal of volatiles [1]. Then, for longer air-blowing times, large molecules formed through condensation and cross-linking. These changes in the chemical structure of the pitch affected the rheological behavior of the pitches.

As Figure 1 illustrates, transient shear experiments performed on these materials following the procedure described in [1] showed that upon inception of steady shear, the parent (untreated) pitch exhibited a purely viscous behavior (no stress overshoot). In contrast, the air-blown pitches showed significant stress overshoot before a steady stress was reached, indicating that these materials were viscoelastic. For air-blowing times up to 25 hours, the stress overshoot increased. This increase in viscoelasticity coincided with the formation of large, aromatic, cross-linked molecules

Controlled-strain oscillatory rheometry was employed to quantify the elasticity of the pitches. The results obtained [1] showed good agreement with those inferred from the transient shear analysis. For example, during the frequency sweep experiments, the phase angle of the untreated pitch remained around 87°, which indicated a nearly pure viscous behavior. In contrast, the viscoelastic nature of the air-blown pitches was evidenced by a phase angle well below 90°.

*Heat-Treated Pitches.* During heat treatment of the parent pitch, the appearance of a disperse anisotropic phase significantly affected the steady rheological behavior of the pitch. While a shear viscosity independent of the rate of shear characterized the isotropic pitches, the liquid crystalline pitch exhibited a shear-thinning behavior at low shear rates. This yield stress was attributed to the mesophase spheres that impeded the flow of the pitch, thereby significantly altering processability.

Similar to the results presented for air-blown pitches, both transient and oscillatory rheometry showed that increasing the extent of heat soaking resulted in a more elastic material. This was probably caused by the polymerization of pitch components during heat soaking, creating long planar elastic molecules.

## Rheology of Liquid Crystalline Pitches

The results of the investigation of the steady shear rheological behavior of mesophase pitches clearly showed that their flow characteristics were similar to that of polymeric liquid crystals (LCPs). Thus a new procedure (based on a technique used for LCPs) was developed in this research for estimating the average elastic constant of mesophase pitches. The determination of these elastic constants allowed a model designed for LCPs to be applied for the first time to mesophase pitches. It accurately predicted their structure shrinkage observed during pure shear flow [2]. Figure 2 shows the good agreement between predicted and measured (by cross-polarized optical microscopy) domain size during shear flow for a selected mesophase pitch.

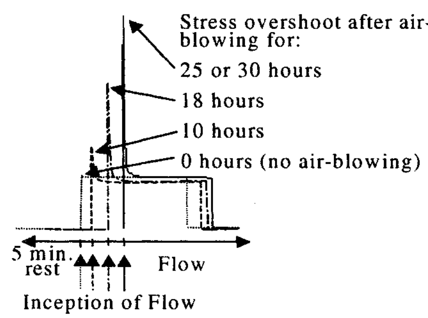


Figure 1. Stress response upon start-up of shear flow for untreated and air-blown pitches [1].

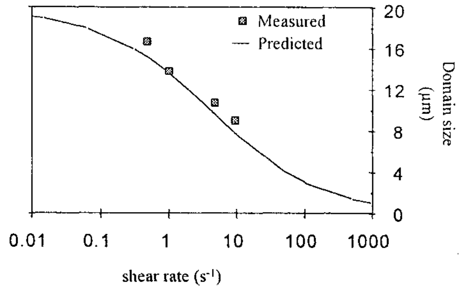


Figure 2. Comparison between predicted and measured domain size during shear flow of a mesophase [2].

## Viscoelastic Flow of Liquid Crystalline Pitches

Observation of pitch samples quenched during extrusion through spinnerette capillaries revealed the peculiar flow behavior of mesohase pitch (refer to [3, 4] for details on experimental procedure). When a flat-entry spinnerette was employed, a vortex developed at the base of the capillary counterbore (refer to Figure 3). This was attributed to the viscoelastic behavior of the mesophase. Profiling the entry section of the spinnerette capillary reduced the size of the vortex and eventually eliminated it (for a 45° entry angle).

Computational fluid dynamics (CFD), widely employed to model the flow of polymers, was used for the first time to model the flow of mesophase pitch. In order to capture the viscoelastic nature of mesophase pitch, its rheological behavior was fitted to the upper-convected Maxwell (UCM) constitutive equation. As Figure 3 shows, using this constitutive equation, it was possible to accurately predict the size of the vortex that appeared at the base of the capillary counterbore. In addition, the predictions from this model agreed with observations of the die swell at the exit of the capillary (see Figure 4).

Finally, this flow model was successfully extended to predict the development of structure during flow of mesophase pitch in the reservoir (upstream from the spinnerette capillary). Even though the region of validity of this model was narrow, it agreed well with the size of the structure experimentally measured in the transverse section of the reservoir, as illustrated in Figure 5.

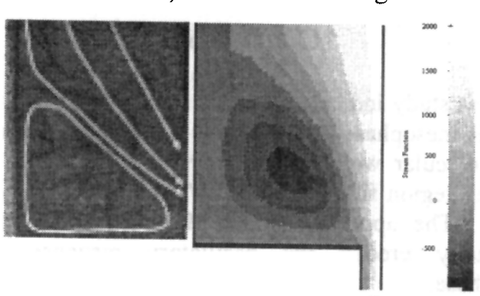

Figure 3. Observed and predicted flow lines as a mesophase extrudes through a flat-entry capillary [3].

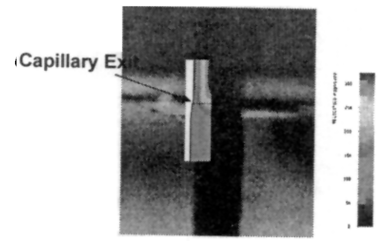


Figure 4. Observed and predicted die swell as a mesophase pitch emerges from a capillary [4].

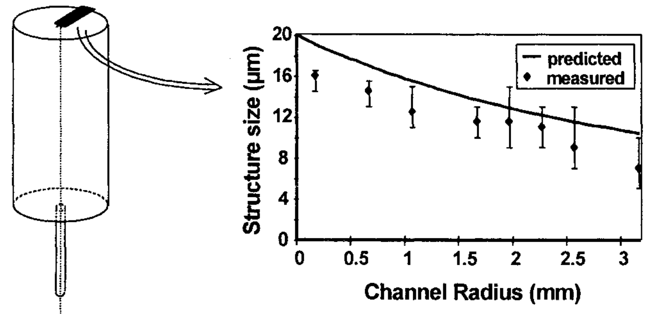


Figure 5. Observed vs. predicted transverse structure in reservoir during mesophase extrusion [4].

## Conclusions

In this work, new transient methods were developed that helped assess the viscoelastic nature of pitches. Also, by extending polymeric liquid crystal theory to mesophase pitch and coupling it to CFD, a method was developed that accurately predicts the development of domain structure during the flow of mesophase pitch. This ability to predict the development of structure lays the foundation for engineering new pitch-based products with designed structures.

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