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Identification of thermal shear bands in a low molecular weight polymer melt under oscillatory strain field

L. Noirez¹ · P. Baroni¹

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Abstract

We present real-time micro-thermal measurements of the response of viscous fluids (low molecular weight unentangled and entangled polymer melts) submitted to an oscillatory mechanical shear strain (in conditions of conventional viscoelastic measurements). We show that thermal changes occur at the early steps of the applied deformation. A succession of thermodynamic states is identified showing the formation of non-uniform temperature shear bands along the strain direction. These thermal shear bands indicate the coexistence of cold and warm zones appearing in phase with the deformation. The synchronism of the temperature variation with the mechanical strain reveals a reversible process of elastic type indicating that viscous liquids might exhibit thermoelastic behaviors.

Keywords Thermoelasticity · Non-uniform temperatures · Shear-elasticity · Liquid melts

Introduction

It is commonly admitted that the mechanical energy injected in a fluid under flow is partly converted into heat by internal viscous friction. In contrast, in nearly static deformation conditions, the mechanical energy is supposed to dissipate in the noise of the thermal fluctuations. The present experimental work reveals actually that the energy is not dissipated by the fluid and that it is possible to identify heating and cooling processes at the earlier steps of the mechanical deformation. The emergence of non-uniform temperatures upon low frequency oscillatory strain in a viscous fluid challenges the standard formalism based on athermal or isothermal equations. The coexistence of cold and hot shear bands evidences processes more complex than the friction heating and introduces the possibility of a stretched state of the fluid in agreement with the excitation of nearly static elastic modes theoretically anticipated [1] and experimentally identified in various fluids first at low scale and then extended to macroscopic scale [2-14].

The identification of (static) shear elasticity in liquids was first revealed in confined fluids at a molecular scale or a multiple of that by designing surface force apparatus [4, 5]. At a micron scale, non-vanishing shear elasticity in liquids was revealed using the atomic vibration of piezomembranes to induce the strain and measure the stress [2, 3]. Using the same principle but at lower frequency and larger scale, a gel-like behavior was reported at 15 µm gap thickness in an untangled polymer in the molten state and was interpreted by a reminiscent effect of the glass transition [6]. X-ray photon correlation spectroscopy showed that an elastic term is needed to model capillary waves of supercooled polypropylene glycol (PPG) [7]. Based on dynamic damping analysis, macroscopic microcrevice measurements show that the viscosity of the fluids is affected by surface and increases as the thickness is reduced [8]. Finally, it was shown that conventional rheometers can get access to the low frequency elasticity up to the sub-millimeter scale by improving the liquid-substrate interaction (total wetting conditions). The sub-millimeter shear elasticity was measured on polymer melts [9, 10] and then extended to glass formers (glycerol, PPG, or OTP), alkanes, ionic liquids, and liquid water [11-14]. These observations carried out on various liquids with different techniques and by different authors indicate a generic elastic property. This ability to respond elastically, i.e., instantaneously to a mechanical excitation, implies that liquid molecules are not dynamically free but long range elastically correlated. This intensity of this collective

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response is ensured by the force of the intermolecular interactions. The low frequency shear elasticity at the macroscopic scale is of fundamental importance to understand the static and flow properties. In particular, such collective property challenges the academic interpretation of the viscoelasticity in terms of single molecular dynamics.

In this paper, we examine the thermomechanical response of a viscous fluid (low molecular weight polymer melt) submitted to a low frequency oscillatory shear strain of variable amplitude. The applied strain conditions correspond to large gap conventional viscoelastic measurements.

It is revealed that the polymer melt exhibits a non-isothermal response even in the low deformation regime (in the so-called viscous (flow) regime). The thermal behavior upon oscillatory field differs from the steady-state flow behavior. Strain-induced thermal shear bands of several tens of micron layers are formed along the strain axis indicating that the increase of the internal energy due to the mechanical strain produces both hot and cold zones. At low strain rates, the temperature variation is reversible and in phase with the mechanical excitation confirming its elastic origin and a possible thermoelastic effect. The establishment of thermal bands challenges the assumption of dissipation in the thermal fluctuation (at low frequency). As a consequence, the thermal study in oscillatory strain field confirms that elastie mechanisms and thus collective intermolecular interactions govern the dynamic response, ruling out an interplay with elementary relaxation times but privileging theoretical approaches based on active defects or extended connectivity [15-18]. Finally and additionally, it is revealed that the high deformation regime of the oscillatory strain is not comparable to a steady-state flow in terms of temperature variation thus justifying separate analysis of the linear and the non-linear rheological approaches.

Materials and methods

The mechanothermal analysis is carried out by recording in realtime oscillatory shear stress and infrared emissivity measurements. We mainly present results obtained on a viscous melt of polybutylacrylate (PBuA) of Mn = 40,000 molecular weight and 1.19 polydispersity. The entanglement threshold is $(Mw \cong 2.Me)$ where Me = 22,000 [19]. The study is carried at room temperature without temperature regulation, i.e., at about 100 °C above the glass transition temperature (Tg = -64 °C) of this amorphous melt, at 0.580 mm gap thickness and using Alumina surfaces as substrate. A comparison is done with a lower molecular weight PBuA (Mn = 25,000 and 1.13 polydispersity index) and with a polybutadiene (PBD) (Mn = 46,700 and 1.11 polydispersity, with an entanglement threshold of Me = $\frac{1900}{100}$. All the samples have been purchased from Polymer Source manufacturer. The oscillatory motion and the shear stress measurement are provided by dynamic mechanical analysis (ARES2 rheometer from TA-Instruments). The dynamic profile is described using the conventional formalism: $\sigma(t) = \sigma_0$. $\sin(\omega t + \Delta \phi)$ with $\sigma(t)$ the shear stress ($\sigma(t)/\gamma(t)$ the complex modulus), $\gamma(t)$ the shear strain (imposed strain mode), and $\Delta \phi$ the phase shift between the input and the output waves, or in terms of shear elastic (G') and viscous (G") moduli: $\sigma(t) = \gamma(t).(G' + i.G")$ where *i* is the imaginary part [7, 9].

The transmission of the stress from the surface to the sample is reinforced by using the excellent wetting procured by the alumina substrate [9]. By strengthening the interaction of the liquid molecules to the surface, the propensity to create interfacial slippage is lowered. Using these high wetting conditions, it has been demonstrated that liquids exhibit a low frequency shear elastic regime prior to the conventional liquid regime [6–14]. Figure 1 displays the stress behavior of the present melt from elastic to flow regime as a function of the shear deformation. At high deformation, the interception of the elastic and the viscous moduli defines the viscoelastic relaxation time which is $\tau_{relax} = 0.03$ s.

The thermal mapping observation is carried out in the (vOz)plane corresponding to the gap plane (Fig. 2). The heat is measured by radiation transfer using the Stefan-Boltzmann law: E = $e_m \sigma A (T^4 - T_c^4)$ where E the radiated energy, e_m the emissivity, A the radiating area, T the temperature of the sample, and T_c the temperature of the surroundings. σ is the Stefan constant. A high performance 320 × 240 pixels B400 FLIR Infra-Red 2D-detector is placed at about 50 mm from the free surface of the sample filling the gap between two wetting substrates made of alumina. The frame rate is 30 Hz. The resolution ellipsoid enables to probe $a \pm 0.15$ mm depth of field. The spectral range goes from 7.5 up to 13 μ m and the temperature accuracy is of ± 0.025 °C. All the files are renormalized by the thermal measurement recorded at rest. The samples are stored at room temperature and an equilibrium time of at least 30 min is observed prior the experiment. The thermal maps are recorded in absolute temperature at room temperature without external thermal input.

Results/discussions

We focus on the low frequency behavior since it characterizes the equilibrium behavior of the fluid, i.e., the dynamic domain where the thermal fluctuations are supposed to be dissipated within the experimental timescale. We probe the thermal response of the polybutylacrylate melt of Mn = 40,000 upon applying variable shear strain amplitudes from 1 up to 1500%. The chosen frequency $\omega = 1$ rad/s (0.16 Hz) corresponds to the flow regime in the frame of a classical viscoelastic description (right inset of Fig. 1). The interception of the loss and the viscous moduli indicates that the longest viscoelastic relaxation time of this low molecular weight melt is $\tau_{relax} = 0.03$ s (right inset Fig. 1). According to the Deborah number (τ_{relax} . $\omega > 1$), no coupling with the viscoelastic relaxation time is possible within the studied low frequency range ($\omega = 1$ rad/s). The thermal measurements are recorded simultaneously to the stress/strain curve (Fig. 1b) ensuring the

Fig. 1 a Scheme of the strain dependence of the shear elastic (G') and the viscous moduli (G'')of a viscoelastic fluid. The upper inset illustrates the strain wave and the stress response corresponding to solid-like and viscous-like waves respectively. The bottom insets illustrate the corresponding frequency dependence for the studied sample (PBuA, Mn = 40,000). The left bottom inset at small strain values displays the shear elasticity, and the right bottom inset displays the conventional viscoelastic curve which is the asymptotic behavior observed at high strain amplitude or large thickness (from [9]). The interception of the viscous modulus and of the shear modulus of the viscoelastic curve provides a terminal viscoelastic time of $\tau_{\rm relax} = 0.03$ s. The zone colored in blue visualizes the strain domain corresponding to the infrared measurements described in details in b (flow regime). b Strain dependence of the viscous and the elastic moduli recorded in situ during the infrared measurements (PBuA, Mn = 40,000, 0.580 mm gap thickness, room temperature environment). The viscous modulus $(G^{"})$ is constant and dominates the elastic modulus, indicating an apparent viscous behavior (flow regime). The vertical bars visualize the strain rate corresponding to the thermal snapshots in Fig. 3



correspondence between thermal and stress measurements. The strain dependence (Fig. 1b) indicates a typical flow regime with the viscous modulus dominating the shear elastic modulus and indicates that the fluid is viscous-like with respect to these strain/ frequency conditions.

The first column of Fig. 3 displays the typical 2D microthermal mapping (snapshots) recorded in the fluid gap upon applying a low frequency oscillatory shear strain (similar mapping are obtained at $\omega = 0.5$ and 2 rad/s being representative of the low frequency behavior). These snapshots indicate that temperature changes are hardly identifiable on instant 2D thermal recording but also that the temperature is homogeneously distributed within the gap (with respect to the strain axis). Because of the temperature homogeneity along the strain axis, it is possible to project the 2D-thermal snapshot data along the gap axis. This 1D representation enables a dynamic analysis illustrated in the second column showing the time dependence of the temperature over one oscillatory period.

The time dependence of the variation of the temperature over an oscillation period (second column) reveals remarkable characteristics:

- Both hot and cold shear bands appear distinctively over 40% strain amplitude. They coexist along the gap (z) and are in phase with the applied strain wave ($\gamma = \gamma_0 \sin(\omega t)$).
- Both hot and cold shear bands are harmonic with the applied strain wave but vary in opposite phase.

Since the (heat and cold) thermal responses are in phase with the applied strain, the change of temperature is linked to elastic wave propagation. In an elastic process, inertia,



Mechanothermal setup

Fig. 2 Scheme illustrating the setup for the simultaneous stress and thermal measurements. The fluid fills the gap between two coaxial alumina disks (of 50 mm diameter). One disk is animated by an oscillatory motion of variable and defined amplitude while the other

disk is fixed producing an oscillatory shear stress of amplitude $\gamma = \delta l/e$ where δl is the displacement and *e* the gap thickness. The infrared sensor is positioned so as to observe the gap in the (*yOz*) plane and records the thermal distribution in the gap

convection, or conduction modes are negligible. In the thermal equation [20, 21], the energy of thermal activation is the following: $\rho.c_v.\frac{\partial T}{\partial t} = T.\frac{\partial \sigma}{\partial T}.\frac{\partial \gamma}{\partial t} + \lambda.\frac{\partial^2 T}{\partial x^2}$ where *T* is the temperature, *t* the time, λ the thermal conductivity, ρ the density, c_v the heat capacity (at constant volume), *x* the position along the displacement axis, σ the stress tensor reduced to a linear component, and γ the strain amplitude approximated to an uniaxial stretching rate.

The first term expresses the thermoelastic effect. The second takes into account the thermal conductivity. Since the thermal bands are nearly in phase with the applied strain, the mechanism does not involve time-dependent conduction or convection mechanisms; the second term is thus negligible. The thermal equation can be simplified to the following: $\rho.c_v.\frac{\partial T}{\partial t} = T.\frac{\partial \sigma}{\partial T}.\frac{\partial \gamma}{\partial t}.$

The stress variation versus temperature is approximately proportional to the linear coefficient of thermal dilatation $(-\alpha)$. Thus, in the frame of an adiabatic approximation, the relationship between the temperature variation and the shear strain is reduced as follows: $\frac{\partial T}{\partial t} = -T \cdot \frac{\alpha}{\rho c_v} \cdot \frac{\partial \gamma}{\partial t}$ (1). This expression typically used for the thermal expansion of solid materials illustrates that the material cools when expanded and heats under compression [20–23]. The expansion ability is related

to the force needed to separate atoms of the material. The situation with polymers is complicated by the competition between intra- and inter-chain contributions together with the possible chain length effect that has a considerable impact for the value of the linear dilatation coefficient [24].

In the present case, since both heat and cold bands are identified under oscillatory strain field, opposite mechanisms are involved. Thus, under oscillatory strain, the polymer melt is subdivided in compressible and dilatation shear waves of several tens microns thick, the compressive wave corresponding to the hot band while the dilatation wave produces the cold band.

Figure 4 illustrates the evolution of the temperature profile along the gap at different strain amplitudes. The thermoelastic origin of the cold band seems to be confirmed since the temperature (peak value) of the cold band evolves nearly linearly with the applied strain in the low strain amplitude regime (up to 100%) in agreement with Eq. (1). The hot band becomes also warmer and compensates the cold part in agreement with instant adiabatic transformation. The thermoelastic mechanism is coherent with the excitation of (collective) elastic mode recently identified in liquids and melts (Fig. 1) [6–13]. In contrast, a coupling with the



< Fig. 3 2D thermal mapping (snapshots) recorded on PBuA melt in room temperature environment upon applying an oscillatory shear strain $\gamma = \delta l l$ e: from **a** to **e**: PBuA Mn = 40,000. **a** $\gamma = 0\%$. **b** $\gamma = 8\%$. **c** $\gamma = 40\%$. **d** $\gamma = 100\%$. **e** $\gamma = 1500\%$. The frequency is $\omega = 1$ rad/s. The dotted lines correspond to the limits of the gap filled with the fluid (e = 0.580 mm thickness, alumina surfaces). The second column shows the evolution of the temperature recorded every 0.04 s and integrated over the gap snapshot along one strain period. The red (●) and dark red (●) points correspond to the lower and upper bands of 5 pixels wide respectively while the blue points (●) correspond to the central band of 5 pixels as indicated by the arrows as indicated on **a**. **f** Evolution of the temperature (recorded every 0.04 s and integrated over the gap snapshot) for the very low molecular weight PBuA sample (Mn = 25,000, polydispersity index: 1.13) along one strain period at $\gamma = 40\%$ and at $\gamma = 100\%$

viscoelastic relaxation time ($\tau_{relax} = 0.03$ s) is not relevant since the fluid would have relaxed within the time of the deformation in the low frequency regime (< 0.1 Hz). The fluid is thus primary thermalized by long-range elastic correlations in agreement with the low frequency shear elasticity (bottom left inset of Fig. 1a).

At high mechanical perturbation ($\gamma > 400\%$ strain amplitude), the thermal measurements indicate an increase of the temperature in the hot band and a decrease of temperature of the cold band of about $\Delta T = 0.30$ °C (Fig. 3e). Additionally, between two oscillations of large amplitude (Fig. 3e), the hot and cold bands do not relax completely. This regime can be interpreted by internal "fracturing" planes of the fluid. In particular, the central cold bands



Fig. 4 Profile of the temperature variation measured along the gap (at the maximum strain value) as a function of the strain amplitude: $\gamma = 0\%$, \Diamond : $\gamma = 8\%$, \blacksquare : $\gamma = 40\%$, \square : $\gamma = 70\%$, \bullet : $\gamma = 100\%$. The inset shows the temperature variation $(T - T_{\gamma=0})$ of the cold (\bullet) and of the hot bands (\blacksquare) as a function of the strain amplitude. Sample: PBuA, Mn = 40,000



Fig. 5 Thermal relaxation after high strain oscillatory stress (PBuA, Mn = 40,000, 1500% strain amplitude, 1 rad/s). **a** Top figure: 2D-thermal mapping of the gap immediately after strain release. **b** Bottom figure: after 80 s. **c** Evolution versus time of the temperature measured in the hot band (**b**) and in a cool band (**+**) upon relaxation

are separated in the middle by a narrow line where the temperature is similar to the temperature at rest (Fig. 3e) and corresponds likely to slippage planes.

At high strain rate (Fig. 3e), the partial thermal relaxation between two successive oscillations observed proves that time scales much longer than the viscoelastic relaxation time ($\tau_{relax} = 0.03$ s) govern the melt in agreement with a possible coupling to elastic modes (i.e., to "infinite" time scales). The coupling with elastic modes is also corroborated with the examination of the relaxation at zero strain. Figure 5 shows the relaxation after applying a high strain amplitude oscillatory motion. A temperature decrease is firstly observed once the strain is stopped (the motion is stopped at the maximum of velocity), followed by a slow temperature increase of the cold part and a slow temperature decrease of the hot part. The timescale to homogenize the temperature in the gap after high strain rate exceeds 80 s which is about 2700 times the viscoelastic time ($\tau_{relax} = 0.03$ s).

Deviations from isothermal behaviors are also observed studying other polymer melts. A twice lower molecular weight PBuA (Mn = 25,000) has been tested in similar conditions of frequency, strain amplitude, and gap thickness. Comparative thermal behavior is observed but higher oscillatory strain rates ($\gamma > 100\%$) are required to reveal a deviation from uniform temperatures (Fig. 3f). The thermomechanical response was also examined with a polybutadiene melt (PBD; Mn = 46,700 (Fig. 6a). Upon large oscillatory strain amplitude, PBD exhibits the formation of hot bands near the wall and of a cool band at the middle gap, similarly as PBuA (Mn = 40,000). In contrast, the steady-state flow measurement of the polybutadiene PBD previously reported in [25] has revealed the formation of a hot central band at shear rates about 100 s^{-1} (Fig. 6b). The thermal behavior upon oscillatory field thus differs from the steady-state flow behavior indicating that the high strain amplitude regime does not reach the asymptotic behavior (continuous flow) justifying a specific analysis of the oscillatory mode.

From the comparison of the different melts, it can be thus established that the molecular mass plays a role and that for the same molecular mass, the degree of entanglements (PDB is a highly entangled polymer compared to PBuA) is also a factor that favors the establishment of non-uniform temperatures.

Conclusions

This pioneering thermal study has enabled the visualization of non-uniform temperatures in a fluid submitted to a low frequency mechanical deformation. Upon applied oscillatory strain, the mechanical energy injected by the strain splits the fluid in several thermal shear bands highlighting the coexistence of both hot and cold bands of nearly equal importance. These local thermal changes are relatively weak (about 0.02 °C in the "thermoelastic" regime up to 0.30 °C in the high strain regime) but they are of importance since they highlight that the injected mechanical energy is not dissipated in the thermal fluctuations challenging the basic assumptions of (athermal) molecular theories.

From low up to about $\gamma < 100\%$, both cold and hot bands respond in phase with the applied strain. This strain-induced effect is a typical thermoelastic effect. Such effects are known in solid materials [20–23] but were so far unknown in the fluidic state since it involves the possibility to change the compressibility (compression and dilatation waves) under relatively moderate stress field.

Cooling challenges also the interpretation in terms of the viscous friction heating (hydrodynamic models only foresee a heating). The obtaining of the coexistence of both cold and hot strain bands involves both compressive and negative pressure states (with respect to the average value). In the cooler zone, the fluid is thus in a stretching state. This expansive state is allowed by supposing that fluids possess static shear elasticity. This is confirmed by recent rheological sub-millimeter measurements [2–14] and theoretical models predicting a non-zero shear length-scale dependence of elasticity or by revisiting



Comparison of the thermal behaviors:

Fig. 6 2D thermal mapping of a polybutadiene (Mn = 46,700 and 1.11 polydispersity) measured **a** under oscillatory shear strain (γ = 1500% and ω = 0.5 rad/s, gap thickness 1 mm). The oscillatory motion induces a central cold band of about – 0.1 °C surrounded by two higher temperature bands similarly as what is observed at low shear rates [5]

and similar to the oscillatory thermal behavior of PBuA (Mn = 40,000). **b** Under *steady-state shear flow* at 100 s⁻¹, the continuous shear flow induces a strong hot central band of about 0.5 °C (see color code and reference [25])

the historical Frenkel zero-frequency shear elasticity to elaborate an alternative solid-like gap-based approach [1, 26].

The present observations have been enabled using highly wetting surface. The fluid/substrate boundary conditions play an important role in rheology while rarely taken into consideration except in very few hydrodynamic models [27]. Because of the shear elasticity, the mechanical energy injected during deformation is partly transformed in non-linear effects of the shear elasticity [28], partly dissipated in particular via fracture/slippage planes separating stretching/compressible states, explaining the absence of chain deformation under steady-state flow in melts [29] or in concentrated solutions [30] corroborated by metastable surface states identified by neutron reflectometry studies [31, 32].

The chain length, the forces of the intermolecular interactions, and the entanglement rate have been here identified as parameters influencing the formation of thermal bands. We are confident that similar thermal effects are present in various fluids and that they have been indirectly detected via ultimate effects like phase separation in solutions, optical banded textures [33, 34], and shear-induced stratification [35]. Therefore, cooling and heating are very likely generic non-equilibrium states of any fluid in motion describing the early steps of the elastic energy dissipation prior its manifestation via conventional stress or optical means [36–39].

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest. The authors are gratefull to Thierry Midaveine for stimulating discussions and acknowlegde the funding provide by the AAP2014 "Instrumentation aux limites" CNRS.

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