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<td>Gan, Hiong Yap; Lam, Yee Cheong</td>
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Experimental observations of flow instabilities and rapid mixing of two dissimilar viscoelastic liquids

Hiong Yap Gan and Yee Cheong Lam

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Experimental observations of flow instabilities and rapid mixing of two dissimilar viscoelastic liquids

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Viscoelastically induced flow instabilities, via a simple planar microchannel, were previously used to produce rapid mixing of two dissimilar polymeric liquids (i.e. at least a hundredfold different in shear viscosity) even at a small Reynolds number. The unique advantage of this mixing technology is that viscoelastic liquids are readily found in chemical and biological samples like organic and polymeric liquids, blood and crowded proteins samples; their viscoelastic properties could be exploited. As such, an understanding of the underlying interactions will be important especially in rapid microfluidic mixing involving multiple-stream flow of complex (viscoelastic) fluids in biological assays. Here, we use the same planar device to experimentally show that the elasticity ratio (i.e. the ratio of stored elastic energy to be relaxed) between two liquids indeed plays a crucial role in the entire flow kinematics and the enhanced mixing. We demonstrate here that the polymer stretching dynamics generated in the upstream converging flow and the polymer relaxation events occurring in the downstream channel are not exclusively responsible for the transverse flow mixing, but the elasticity ratio is also equally important. The role of elasticity ratio for transverse flow instability and the associated enhanced mixing were illustrated based on experimental observations. A new parameter \( D_{\text{ratio}} = \frac{D_{\text{side}}}{D_{\text{main}}} \) (i.e. the ratio of the Deborah number \( D_e \) of the sidestream to the mainstream liquids) is introduced to correlate the magnitude of energy discontinuity between the two liquids. A new \( D_{\text{ratio}}-D_{\text{main}} \) operating space diagram was constructed to present the observation of the effects of both elasticity and energy discontinuity in a compact manner, and for a general classification of the states of flow development. Copyright 2012 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4768667]

I. INTRODUCTION

Liquid flow in microfluidic channels tends to be laminar due to the low Reynolds number \( (Re < 1) \) associated with its microscale dimensions. For a simple straight channel it is nearly impossible to induce a chaotic microfluidic flow that requires high \( Re \). However, chaotic/turbulent flow is a much sought after mechanism for mixing because it not only provides rapid mixing but allows timely and complete reactions. One of the simple ways of achieving rapid mixing is to introduce an elastic force in additional to the usual viscous and inertial forces in a microfluidic system. This approach would have the potential to disturb the liquid from its laminar regime and bypass the inherent small \( Re \) limitation.

Aqueous solutions of flexible polymers are viscoelastic. The distinct characteristic of a viscoelastic liquid is its strong dependency of elastic stresses on the flow history. When the flow stops,
these stresses will decay over a period of time due to the relaxation of polymer coils to its equilibrium state, known as polymer relaxation time ($\lambda$). Conversely these stresses would be increased non-linearly when the flow characteristic time ($t_{flow}$) is comparable with $\lambda$ of a viscoelastic liquid. In other words, for a liquid with large $\lambda$, the induced stresses will relax slowly and the elastic effects are prominent even at a low deformation rate. While for a liquid with small $\lambda$, significant elastic effects can also be exhibited provided that the imposed deformation rate is sufficiently high. Thus, both solution characteristic time (relaxation time) and flow characteristic time (e.g. the inverse of the deformation rate) are indeed key parameters dictating the viscoelastic response of a viscoelastic liquid. Intrinsically, viscoelastic liquids allow flow fields and instabilities associated with these elastic effects to be excited via short length and time scales of a flow.$^4$–$^6$ If $t_{flow}$ is shorter than $\lambda$, the residual elastic stresses stored in the liquid can result in the development of secondary flows and instabilities, subjected to a dedicated flow geometry.$^4$–$^5$ Hence with microdevices, manifestations of elastic effects and instabilities that are difficult to achieve in macrodevices can be explored in the absence of inertia. Such phenomena are practically independent of Reynolds number (Re), but strongly dependent on Deborah number, $De = \lambda \times (t_{flow})^{-1}$. The relative dominance of elastic to inertial effects in a viscoelastic flow is dictated by the definition of Elasticity number ($El = De/Re$). Furthermore, to exploit effectively the viscoelasticity of such liquids for elastic flow instability, abrupt and sharp convergent/divergent geometries should be employed.$^3$–$^8$ It is known that rounded corners will compromise the elastic effects.$^9$–$^{10}$ This is attributed to the stress singularities developed at the entry corners which have been well documented as the source of elastic instabilities in many macroscale experiments.

It was recently reported that the viscoelastic characteristic in a liquid was manifested through the length scales and timescales of the associated flow which led to pure elastic flow instability.$^7$–$^{11}$–$^{14}$–$^{18}$ and even elastic turbulence where efficient mixing was achieved on a micro-lengthscale.$^{15}$–$^{18}$ However, the majority of investigations were focused on the flow dynamics of a single or two similar viscoelastic liquids. Little attention had been given to the flow development of a system with dissimilar viscoelastic liquids (i.e. at least a hundredfold different in shear-viscosity of the two liquids). In fact, such multiple-phase flow system is also equally important in both engineering and biological applications.$^1$–$^3$–$^{19}$–$^{20}$ For instance, phosphate concentration detection in water quality diagnosis involving the mixing of a sample and viscous reagents.$^{21}$–$^{22}$ In polymer and chemical syntheses micro-reactors,$^{23}$–$^{25}$ dissimilar viscosities could significantly influence the reaction rate. Other applications like rapid mixing of crowded biological solutions,$^{26}$–$^{27}$ (e.g. highly concentrated protein or enzyme solutions) and injecting of reagent into whole blood$^{28}$ also require the mentioned domain knowledge to achieve a precise incubation period and rapid-mixed samples.

With high molecular weight and flexible chain polymers, we have recently demonstrated that convective/transverse flow instabilities could be obtained via abrupt planar contraction-expansion microchannels in a multi-phase flow system (a miscible liquids system).$^2$–$^{29}$ These instabilities result from the unequal relaxation of elastic stresses stored in the fluids, after severe stretching thru the contraction channel.$^9$–$^{10}$ These instabilities can provide rapid microfluidic mixing at a short mixing length ($< 5$ mm).$^2$–$^{29}$ Furthermore, the unique advantage of this mixing technology is that the viscoelastic properties responsible for elastic flow instabilities could be readily found in most chemical and biological samples like organic and polymeric solutions,$^{23}$–$^{25}$ blood$^{28}$ and crowded proteins and enzymes samples.$^{26}$–$^{27}$

In this paper, we used the same microdevice previously reported$^2$,$^3$ to experimentally show that the viscoelasticity ratio (between mainstream and sidestream liquids) has a direct bearing on the magnitude of the induced elastic flow instabilities, and in particular the transverse flow instability at downstream of a contraction. The possible underlying mechanism is discussed to elucidate the complex interplay between elasticity/viscosity and the elasticity ratio between the mainstream and side-streams solutions. Dependence was observed in the measured enhancement of the mixing quality to the magnitude of the induced elastic flow instability, which was a function of the ratio of the elasticity of the two solutions. A new parameter $De_{ratio} = De_{side} / De_{main}$, i.e. the ratio of $a$The flow characteristic time ($t_{flow}$) was interpreted as the ratio of the system characteristic dimension to the flow velocity.
FIG. 1. (a) Device schematic for 8:1:8 contraction ratio. Arrows depict the flow direction where green and red colors represent mainstream and sidestream liquids respectively. \( w_c \) is the contraction channel width and \( L_{\text{char}} \) is the upstream channel width. (b) Particle streak flow sequence snapshots for a flow system with 1\%PGW (mainstream) and 0.1\%PW (sidestream) at 10 ml/hr. The shots were captured at a time interval of 2.4 seconds. 3-μm particles were seeded in sidestream liquid at a ratio of 1:10. (c) Close-up flow visualization at contraction channel with fluorescent particle streak and green fluorescent dye flows at 10 ml/hr.

The Deborah number (De) of the sidestream to the mainstream liquid, is introduced to correlate the magnitude of the energy discontinuity between the two liquids. A new Deratio-De\(_{\text{main}}\) operating space diagram is constructed to map in a compact manner the observation of the effects of both elasticity and energy discontinuity. In addition, the dynamic flow development of two dissimilar viscoelastic liquids (with flow visualization) is also captured and characterized in this space diagram.

II. EXPERIMENT

A. Device Geometry

The abrupt planar contraction/expansion microchannel (1 mm: 125 μm: 1 mm in width, namely 8:1:8 contraction ratio) of 150 μm in average depth was first etched in silicon wafer using Deep Reactive Ion Etching (DRIE). The microchannel was then sealed with Pyrex glass via anodic bonding. Multiple-stream flow (i.e. 3-stream flow) consisted of a more viscoelastic mainstream in the centre and two less viscoelastic sidestreams (with one sidestream introduced from each side of the device), see Fig. 1. The volume flow rate for the mainstream to each sidestream liquid was kept constant at a ratio of 1:0.5. The two test liquids were delivered by a precision pump (Lomir Biomedical Inc.) via Hamilton GASTIGHT glass syringes. The total volumetric flow rate of the system was \( \dot{Q} \).

B. Flow Visualization and Mixing Measurement

Experiments were performed over a range of 40 < El < 8000 and 15 < De\(_{\text{ratio}}\) < 70 by varying the polymer concentration (c) and flow rate (\( \dot{Q} \)). A similar optical setup (Supplementary information, Fig. S1)\(^{10}\) and mixing evaluation algorithm (Supplementary information, Eq. (1))\(^{30}\) as reported in our previous papers were employed to visualize the flow and to evaluate the mixing quality. In brevity, fluorescent intensity images were captured with a CCD camera by adding a fluorescent dye, Fluorescein Disodium (Sigma Aldrich), to PGW (mainstream liquid) at a weight ratio of 0.0003:1, which was illuminated by a mercury (Hg) lamp with an epi-fluorescent attachment. Fluorescent
TABLE I. Fluid composition and rheological properties of test samples. All measurements were recorded at 24 ± 1°C.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>(c/c*)c</th>
<th>ρd [kg/m³]</th>
<th>ηo[e][mPas]</th>
<th>λf[f][ms]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1% PWb</td>
<td>0.898</td>
<td>997 ± 10</td>
<td>2.24 ± 0.3</td>
<td>1.537</td>
</tr>
<tr>
<td>0.3% PW</td>
<td>2.693</td>
<td>990 ± 10</td>
<td>8.0 ± 0.4</td>
<td>4.437</td>
</tr>
<tr>
<td>1% PGWb</td>
<td>8.977</td>
<td>1137 ± 20</td>
<td>903 ± 100</td>
<td>103 ± 6</td>
</tr>
<tr>
<td>0.8% PGW</td>
<td>7.181</td>
<td>1133 ± 20</td>
<td>402 ± 50</td>
<td>64 ± 5</td>
</tr>
</tbody>
</table>

aPolyethylene oxide (PEO) in water with 3 μm microspheres is denoted as PW. Percentage (%) represents the weight percentage of PEO content.
bPEO in 55 wt% glycerol water mixture with fluorescence dye is denoted as PGW.
c and c* are the polymer concentration and polymer overlap concentration respectively.
dρ is the fluid’s density.
eηo is the zero-shear viscosity (the rheological measurements were shown in Fig. S2).f
fλe is the extensional relaxation time measured by Haake CaBER1 extensional rheometer (the measurements were presented in Fig. S3).

streak flow imaging was used to characterize the flow kinematics associated with a steady and time-dependent two-dimensional flow. Streakline imaging was facilitated by adding an aqueous solution of 3 μm red fluorescent particles (Duke Scientific) to PW (sidestream liquid) at a volume ratio of 0.1:1. 3-dimensional effects on flow development are not covered and discussed in this paper as 3D effects were considered to be negligible in this study because the vertical gradients of the horizontal flow velocity are negligible.

C. Fluids and Rheology

Mainstream liquids were prepared by adding 0.1, 0.6, 0.8, or 1 wt% of 2 × 10^6 Da polyethylene oxide (PEO, The Dows Chemical Co.) to 55 wt% glycerol in de-ionized (DI) water, and were denoted as PGW. Sidestream liquids were prepared by adding 0.1 or 0.3 wt% PEO to DI water, and were denoted as PW. Neighbouring polymer coils will impinge on each other at an overlap concentration c* of ~1100 ppm for the PEO used. The rheological properties of the test liquids are tabulated in Table I. All the test solutions, (together with the added additives, namely fluorescence dye in mainstream fluids and fluorescent micro-particles in side-stream fluids) were measured and characterized (Supplementary information, Fig. S2 and Fig. S3). Due to the limitation of the rheological equipment, the extensional rheological properties of the sample fluids in the dilute regime, i.e. 0.1% PWS and 0.3% PWS, could not be characterized directly with our existing facilities. Therefore, their values were taken from measurements reported by Rodd (Ref. 36). We understand that CaBER relaxation time has to be measured experimentally due to its sensitivity to solution preparations. Thus, extracting these relaxation times from the literature will deem the results unsatisfactory, in particular to map out a precise flow transition in microfluidic channels. Herein, we used the same raw material and prepared the same viscosity (Contraves LS 40) with < 5% variation in measured values. As a result, the relaxation time of the actual samples should not differ significantly from reported values. In addition, as dilute solutions were assumed to be largely relaxed before discharging out of the contraction channel, the deviations of the actual properties would have little impact on the experimental observations (more details will be discussed in section III).

D. Dimensionless Parameters

The actual flow conditions in the contraction channel (e.g. flow velocity) of each individual stream were not recorded due to technical difficulty in capturing flows at very high speed (e.g. in meter per second of sidestream flow). Instead, we estimated the average flow velocities of the individual streams within the contraction based on the assumption that the correlation of wetted-area ratio of two streams is proportional to the viscosity ratio of these two liquids.
The contraction/expansion flow experiments were characterized in terms of the Reynolds number (Re), Deborah number (De), and the Elasticity number (El). Peclet number (Pe) was also included to show the dominant transport phenomenon in such flow system. The same notations were used here as in our previous work\textsuperscript{2,3} that is all lengthscales and velocity terms are associated with the contraction channel, unless otherwise stated.

The Deborah number is defined in terms of the characteristic shear rate ($\dot{\gamma}_{\text{char}}$) in the contraction channel as,

$$De = \lambda_e \dot{\gamma}_{\text{char}} = 2\lambda_e \bar{U}_{\text{ave}} / L_{\text{char}}$$

where $\dot{\gamma}_{\text{char}} = \bar{U}_{\text{ave}} / (L_{\text{char}} / 2)$, $\bar{U}_{\text{ave}}$ is the average velocity, $\lambda_e$ is the relaxation time measured with an extensional rheometer (Haake CaBER), $L_{\text{char}}$ is the characteristic length which is the channel depth ($d$), and $\dot{Q}$ is the total volumetric flow rate.

The Reynolds number is defined as,

$$Re = \rho \bar{U}_{\text{ave}} L_{\text{char}} / \eta_o$$

in which $\rho$ is the liquid density and $\eta_o$ is the zero-shear viscosity.

The Elasticity number is expressed as,

$$El = De/Re$$

The Peclet number is given by,

$$Pe = \dot{Q} W_{\text{char}} / D(w_{\text{e}}d)$$

in which $W_{\text{char}}$ is the upstream channel width and $D$ is the diffusion coefficient. Since the diffusion coefficient is inversely proportional to the fluid’s viscosity,\textsuperscript{24} we estimated that $C = 1.66 \times 10^{-12}$ m$^2$/s and $3.73 \times 10^{-12}$ m$^2$/s for 1% and 0.8% PGW respectively based on the $D$ of dye in water ($\sim 1.5 \times 10^{-9}$ m$^2$/s in Ref. 3). A smaller $D$ indicates that diffusive mixing mechanism is less significant.

A smaller channel has smaller flow characteristic length and time. Thus, Re is smaller with a stable inertia/viscous flow. Conversely, De becomes larger and it is easier to have elastic/viscous instability. The dominance of the spatial lengthscale and its effects on fluid elasticity is dictated by the Elasticity number (El), which characterizes the ratio of fluid elasticity to fluid inertia. El is a constant for a given fluid and channel geometry. In this paper, with the mainstream fluid as the reference, the experiments were conducted over the range of $5.2 < De_{\text{main}} < 122.4$, $0.003 < Re_{\text{main}} < 1.4$, and $37.1 < El_{\text{main}} < 7.0 \times 10^3$. The $El_{\text{main}}$ values attempted here are typically not accessible in the equivalent macro-scale experiments.\textsuperscript{7} Thus, the mainstream flow regime investigated has negligible inertial effects and can be characterized by De alone. Furthermore, the Pe value was found to be at least (O $\sim 10^4$) in all experiments indicating that transport means by molecular diffusion is insignificant.

### III. RESULTS AND DISCUSSIONS

Fig. 1(b) presents a highly unstable flow (it was a typical flow pattern in unsteady vortex growth with viscoelastic flow instability regime shown in Fig. 2). Based on this flow, we will first describe the flow journey of polymer coils within the mainstream liquid as an appropriate reference point. As shown in Fig. 1(a), at locations upstream of a contraction prior to the 3-stream intersection point, polymer coils were first subjected to a relatively mild deformation (or stretching) in the planar device. This deformation was mainly imposed by the shearing flow associated with the planar micro-geometry. As polymer coils flowed pass the stream-intersection point, they experienced a large and fast extension generated by the converging flow near the contraction entrance, whereas the shearing deformation at this point is relatively small except at the interface between the main and side streams. When the polymer coils entered into the contraction channel, they experienced a high shear flow over the period of its flow residence time, see Fig. 1(c). Three important events took place inside the contraction: relaxation of polymer after the upstream extension, “tumbling” due to the hydrodynamic drag which decreased as the polymer aligned and started to relax,\textsuperscript{35} and a
second elongation imposed by the high shear flow. In addition, this contraction flow determined the magnitude of the stored elastic energy to be released (relaxed) at the downstream channel by these highly stretched polymers (by extensional, shear and strain history). Lastly, at locations downstream of the contraction, the polymer relaxation events were strongly coupled to the downstream expansion effects. The huge difference in the stored elastic energy of the mainstream and sidestreams allowed the mainstream liquid to exert a strong transverse flow through the release of the elastic energy on exit of the contraction and to displace the weaker sidestream liquids next to it. This hypothesis was made on the basis of a strong elastic flow instability observed at downstream of a contraction (see Fig. 2 and 3) and rapid mixing of liquids with negligible diffusion.2, 29

Based on the experimental observations, the distinct flow patterns were summarized in a $\text{De}_{\text{ratio}}$-$\text{De}_{\text{main}}$ space diagram in Fig. 2. This is the first ever attempt to propose a new parameter $\text{De}_{\text{ratio}}$ and the associated space diagram for providing a compact holistic view of the flow development of a multiple-phase viscoelastic flow system. The existence of various flow regimes was also shown for the first time in an abrupt planar contraction/expansion microchannel. Four distinct flow regimes have been identified based on the change in streamlines at locations upstream of contraction. These are the steady Newtonian-like flow (laminar streamlines), onset elastic instability (bending and diverging streamlines), lip vortices and stable symmetric vortex growth (formation and growth of lip vortices) and unsteady vortex growth with viscoelastic flow instability (salient corner vortices collapse and re-build). Similar flow regimes for a single viscoelastic liquid on the microscale have been previously reported.7 However, here the regime boundaries could not be precisely identified, in particular for flow transition. However, this would not compromise the overall trend and conclusion reached in this investigation.

In Fig. 2, flow regimes are separated by blue colored slanted dashed-lines (regime boundaries) in the $\text{De}_{\text{ratio}}$-$\text{De}_{\text{main}}$ space. The slanted boundaries show the strong dependency of both $\text{De}_{\text{main}}$ and $\text{De}_{\text{ratio}}$ in the course of flow development. As shown in this space, the critical $\text{De}_{\text{main}}$ for the
inception of each flow regime decreased as De\textsubscript{ratio} was increased. Similarly, the De\textsubscript{main}/flow rate required to trigger elastic instabilities decreased with increasing De\textsubscript{ratio}. The larger the De\textsubscript{ratio}, the lower the deformation rate required to trigger the elastic instability. Consequently, the required level of un-relaxed elastic energy discontinuity between these two liquids at locations downstream of contraction was much easier to attain.

Fig. 3 illustrates the transition across the various flow regimes for a fixed De\textsubscript{ratio} (~ 4.2, refer to data points in the red box of Fig. 2) with increasing flow rate. In steady Newtonian-like flow regime (refer to Fig. 3(a)), the 3-stream flow exhibited laminar flow behavior. At this low De flow state, the dominance of viscous forces resulted in the three streams flowing through the abrupt contraction/expansion like highly viscous Newtonian liquids. The fluids upstream of the contraction converged in a laminar fashion and accelerated directly towards the contraction. The entire flow field was observed to be stable and steady throughout. With increasing flow rate, elastic effects in the flow became apparent; on entering the onset elastic instability flow regime, a dramatic change in the shape of the streamlines was observed (see Fig. 3(a) and 3(b)). Elastic instability was initiated at the re-entrant corner (corner at contraction entrance), and the flow field no longer monotonically converged towards the contraction. Bending and diverging streamlines were observed near the centerline. At locations downstream of the contraction, the flow streams were visibly stable and steady with some waviness of stream-stream interfaces (not shown in the figure). At higher flow rates, i.e. in the lip vortices and stable symmetric vortex growth regime, the formerly diverging and bending streamlines
developed into an intense vortex (lip vortices) at the re-entrant corner. As $D_{\text{main}}$ increased, the lip vortices increased in size and extended toward the channel corners. Eventually, the lip vortices filled the entire upstream contraction plane (channel wall between the upstream channel and the contraction). The flow entered the stable symmetric vortex growth regime in which an increase in $D_{\text{main}}$ led to a rapid increase in vortex size towards upstream (see Fig. 3(c) and 3(d)). At locations downstream of the contraction, these three distinct upstream flow streams were laminated into more streams with the onset of elastic instability. As the flow rate increased further, these laminated flow stream interfaces transitioned from a wavy pattern to an intensified dynamic up-down swinging (see Fig. 3(d)). Furthermore, there was visible penetration of the sidestream liquids into the central portion of the channel, overlapping with the mainstream fluid. These penetrated-streams fluctuated intermittently in location and did not fully extend across the whole downstream channel width. Finally, with an increase in flow rate into the unsteady vortex growth regime, the salient corner vortices at locations upstream of contraction reduced in size abruptly and became unstable and unsteady in nature (see Fig. 3(e)). One or both sides of the corner vortices collapsed (vanished) randomly and caused repeated “swinging” of the flowing mainstream liquid (viscoelastic whipping) across the channel width. However, no perceptible change of behavior at locations upstream of contraction was observed as the flow rate was further increased.

Viscoelastic flow fluctuation was observed to be more significant at locations downstream of a contraction, which was aligned with our previous micro-particle image velocimetry ($\mu$-PIV) measurements. This was due to stress relaxation of the highly stretched polymer coils after being flushed through the contraction at high speed. Significant elastic whipping at locations upstream of a contraction not only caused fluctuations in the mainstream flow but also created a chaotic flow resistance to the sidestreams entering the contraction. These fluctuations resulted in severe flow instability at locations downstream of contraction. Prominent cross-stream interactions were promoted and extensive overlapping (or penetration) of streams was observed. Further increase in $D_{\text{main}}$ did not intensify cross-stream interaction at locations downstream of contraction, but a suppression of cross-stream interaction was observed [see Fig. 3(f) and 3(g)]. This could be attributed to the delayed relaxation process of a higher viscoelastic liquid (mainstream PGW) due to a reduced flow residence time. The stretched polymer coils were flushed past the analysis window before their relaxation effects could be observed. This hypothesis was later supported by the corresponding mixing performance presented in Fig. 5.

As earlier defined, $D_{\text{ratio}}$ is a measure of the un-relaxed elastic energy discontinuity between the two liquids as they exit the contraction. This can be explained by examining the relaxation status of each stream at the exit of the contraction. A simple Maxwell liquid stress relaxation model was adapted to estimate the relaxation status,

$$\Gamma_{\text{rel}} = 1 - e^{-t_{\text{res}}/\lambda_{e}} \tag{5}$$

where $t_{\text{res}}$ is the flow residence time and $\lambda_{e}$ is the extensional relaxation time measured using the Haake CaBER 1 rheometer. The magnitude of this dimensionless $\Gamma_{\text{rel}}$ represented the proportion of residual stresses in the streams as they exited the contraction. For instance when $\Gamma_{\text{rel}}$ approaches unity, sample fluids experienced little relaxing. Conversely when $\Gamma_{\text{rel}}$ approaches zero, sample fluids relaxed almost completely.

The flow residence time may be estimated by,

$$t_{\text{res}} = L_{c} \bar{U}_{\text{ave}}^{-1} \tag{6}$$

where $L_{c}$ is the length of the contraction and $\bar{U}_{\text{ave}}$ is the average velocity in the contraction.

The single mode Maxwell characterization of the solutions adopted here is a simple model which might not capture completely the underlying physics of the complex viscoelastic responses, such as large elastic normal stresses, bending streamlines, onset lip vortices etc. This simple model, however, is adequate to facilitate the explanation of un-equal relaxation of these two liquids and the corresponding transverse flow instability downstream of a contraction.

During convergent flow from upstream to the contraction, both the main and side streams underwent significant shear and extensional flows. However, due to its much higher viscoelasticity, the main stream will have much higher stored elastic energy. As stated previously, without any
FIG. 4. The relaxation status of sample fluids ($\Gamma_{rel}$) at exit of the contraction versus total flow rate. When $\Gamma_{rel} \to$ unity, sample fluids experienced little relaxing and when $\Gamma_{rel} \to 0$, they relaxed almost completely. Data were calculated based on flow cases of 1wt% PGW with 0.1wt% PW ($\text{Deratio} = 5.9$) and 0.8wt% PGW with 0.3wt% PW ($\text{Deratio} = 2.2$).

relaxation, $\text{Deratio}$ may be used as a measure of the elastic energy discontinuity between the main and side streams as they exit the contraction. In addition, as shown in Fig. 4, minimal relaxation ($< 20\%$) can be observed for both main and side streams in the contraction, especially at high flow rates ($> 10 \text{ ml/hr}$). As such, the energy discontinuity between the main and side streams remained and had not relaxed significantly. As the liquid exits the contraction, especially at higher flow rates, i.e. higher $D_{\text{main}}$, the sudden loss in physical constraint resulted in a substantial amount of stored elastic energy released quickly from the mainstream liquids as compared to the side streams. Thus, as observed in our experiments at locations downstream of the contraction, this substantial amount of elastic energy released from the mainstream liquid induced a strong transverse flow and displaced the relaxed sidestream liquids next to it. This resulted in a strong elastic flow instability observed downstream of the contraction and therefore an effective mixing of the two dissimilar viscoelastic liquids with negligible diffusion and inertial effects.\(^2\)\(^,\)\(^29\) In addition, the lower $\Gamma_{rel}$ for 0.8% PGW (see Fig. 4) provides further explanation for the slanted regime boundaries in Fig. 2, i.e. increased $D_{\text{main}}$ required for flow regime transition at lower $\text{Deratio}$.

The performance of mixing enhancement through viscoelastically induced multiple-stream flow instability of two dissimilar viscoelastic fluids can be similarly characterized in the $\text{Deratio}-D_{\text{main}}$ space as shown in Fig. 5. The detailed mixing quality quantification is presented in Supplementary information.\(^30\) The noticeable effects of $\text{Deratio}$ and $D_{\text{main}}$ associated with the induced mixing enhancement are clearly illustrated in the $\text{Deratio}-D_{\text{main}}$ space. From Fig. 5, mixing was observed to be relatively low in the Newtonian-like flow regime ($\approx 25\%$). By comparing the red hexagon data points, there was an abrupt improvement in mixing when crossing from this regime to the onset instability flow regime with mixing performance achieving $\approx 40\%$ except those at very low $\text{Deratio}$. Subsequently, the improvement in mixing performance was gradual when $D_{\text{main}}$ increased further, and the flow regimes progressed to symmetric vortex growth and chaotic instability flow regimes. Mixing performance was observed to improve significantly ($\approx 60\% \sim 70\%$) at relatively large $\text{Deratio}$. However, Fig. 5 indicates that even for a constant high $\text{Deratio}$, there was only a mild increase in mixing performance as $D_{\text{main}}$ increased. These results show that $\text{Deratio}$ is the more significant parameter in dictating enhanced mixing, as compared with $D_{\text{main}}$. This is expected because $\text{Deratio}$,
being a measure of the elastic energy discontinuity between the streams at the contraction exit, affects the inter-penetration of one stream into the other and hence directly affects the degree of mixing.

It is highlighted here that, for a fixed window of observations, the interplay between the energy of discontinuity and the duration of travel (directly proportional to the relaxation status of deformed polymer coils) confounded somewhat the mixing analysis. As shown in Fig. 5, these two factors at slow and moderate flow rates demonstrated an increased in mixing with increasing flow rate. This observation was aligned with our hypotheses as the total elastic energy discontinuity increased with flow rate. However, in order for this elastic energy discontinuity to effect mixing, the elastic energy must be released (relaxed) to cause the mainstream fluid to penetrate the sidestreams.

To estimate the remaining degree of relaxation at a specific location with respect to the contraction exit, eq. (5) is modified with an additional time constant $\Delta t$,

$$ (\Gamma_{rel})_{out} = 1 - e^{-(t_{res}+\Delta t)/\lambda_e} $$

where $\Delta t$ is the travelling time of the stream of interest to a finite location from the exit of the contraction.

The remaining degree of relaxation $(\Gamma_{rel})_{out}$ is computed at 1.5 mm downstream (location of the observation window) of the contraction (Supplementary information, Fig. S4). At slow and moderate flow rate (i.e. low $De_{main}$), the stored energy of the streams flowing past the observation window was allowed to relax more than 80% (i.e. $1 - (\Gamma_{rel})_{out}$) to result in an effective mixing when the streams flowed past the observation window. However, mixing at the observation window at higher flow rates decreased (despite of higher stored energy) due to insufficient polymer relaxation, in particular at the chaotic flow instability regime. In other words, with the same time constant for a viscoelastic solution, a longer travelling distance is required for the deformed polymer coils to relax back to the same extent at a faster flow rate. Comparing with Fig. 5, we found that to have effective mixing, the mainstream would have released (relaxed) more than 80% of its stored elastic energy in order to generate significant stream-stream interactions.
Consequently, there were a few “unexpected” data points with a reduction in mixing performance with increasing De_{main} and/or De_{ratio} (shown in red dotted boxes in Fig. 5). These data points are physical experimental observations and not artefacts. These observed mixing reduction indeed was not an actual reduction in mixing performance, but mainly a manifesto of the close proximity of the location of the analysis window with respect to the contraction. The induced flow instabilities were compromised by the lower degree of relaxation at the observation window due to the faster flow rates of the streams. As such, these data points should not be used for final mixing performance evaluation as its lower mixing performance is caused by an additional mechanism as compared to the other data points. Indeed, although lower mixing was observed at the location of observation window at these higher flow rates, it can be reasonably expected that at further downstream where more relaxation had occurred, mixing would have increased.

IV. CONCLUSIONS

Based on experimental observations, a De_{ratio} – De_{main} operating space for characterizing the dynamical flow behavior and mixing efficiencies of a multiple-stream (i.e. 3-stream) viscoelastic flow was established. This is the first ever attempt to propose a new parameter De_{ratio} for the characterization of such flow in a compact space diagram, providing a holistic view of the dynamical flow development and its resultant behavior. The existence of various flow regimes was demonstrated and indentified in terms of the effects of both elasticity and energy discontinuity. The degree of mixing corresponding to the flow kinematics was found to depend significantly on De_{ratio}, which is a measure of the viscoelastic energy discontinuity between the two viscoelastic liquids. This De_{ratio} and De_{main} space is expected to be a useful tool for multiple-stream flow of dissimilar viscoelastic liquids and has the potential to provide a framework for quantitative investigations of the mentioned flow system.

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30 See supplementary material at [http://dx.doi.org/10.1063/1.4768667](http://dx.doi.org/10.1063/1.4768667) for additional figures and measurements on both rotational and extensional rheological measurements, remaining degree of relaxation ($\Gamma^{\text{rel}}_{\text{out}}$) of samples fluids at various flow rate.