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Microfluidic behaviour of perfluoropolyether fluids in poly(dimethylsiloxane) micro-channels

Ilenia Viola [a], Giuseppe Ciccarella [a], Pierangelo Metrangolo [b,*], Giuseppe Resnati [b,**], Roberto Cingolani [a], Giuseppe Gigli [a,***]

[a] *National Nanotechnology Laboratory (NNL) of CNR, INFM, Distretto tecnologico ISUFI and Dipartimento di Ingegneria dell'Innovazione, Università degli Studi di Lecce, via Arnesano, I-73100 Lecce, Italy*

[b] *Nanostructured Fluorinated Materials Laboratory (NFMLab), Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Politecnico di Milano, via Mancinelli 7, I-20131 Milano, Italy*

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Abstract

Two different perfluoropolyether-based fluids, namely the unfunctionalized GALDEN SV90® and the dihydroxy derivative FOMBLIN Z-DOL® 2000 were employed as liquid samples in a poly(dimethylsiloxane) (PDMS) microfluidic setup, fabricated by soft-lithography techniques. The results of our investigation were compared with the behaviour of the low viscosity and high-fragility polyurethane structural adhesive (NOA72®), that is well known as an excellent material for the fabrication of sub-micrometer structures by soft-lithography techniques, and whose structural elastic properties inside restricted geometric systems have been recently investigated.

Keywords: Perfluoropolyethers; Microfluidics; Surface effects

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1. Introduction

Much effort has been directed to the study of the properties of solid–liquid interface during the displacement of liquids inside geometrically restricted structures. A fine control of the dynamics in a microfluidic setup seems to be a prevalent tool to effectively address manifold operations inside integrated fluidic circuits (i.e. lab-on-chips, LOCs). Because of the profound influence that the fluorine-containing liquids can have upon the physical and chemical properties at the interface [1], we have employed two different perfluoropolyether-based fluids, available under the trade name GALDEN SV90® and FOMBLIN Z-DOL® 2000 (Solvay-Solexis), as liquid-samples inside a poly(dimethylsiloxane) (PDMS) micro-channels structure.

GALDEN SV90® (CF_3–[$(OCF_2CF_2CF_2)_m$–$(OCF_2)_n$–]OCF_3) is mainly employed for its thermal resistance, non-toxicity, excellent dielectric properties, no flash or fire point and low viscosity. Typical applications include heat transfer, electronic reliability testing and coatings [2]. FOMBLIN Z-DOL 2000® ($HOCH_2CF_2O$–$(CF_2CF_2O)_p$–$(CF_2O)_q$–CF_2CH_2OH) is a high performance lubricant with applications in the chemical, electronic, nuclear and data processing industries [3]. Details of the material properties are reported in Table 1.

In the last years, PDMS surface chemistry has been gaining increasing attention because of its potential applications especially in the diagnostic industry, where PDMS is the main component for the realization of micron and nanometre structures over a large area inside functional integrated devices [4,5]. In general, the investigation of the fluid-dynamics properties in micro and nano-channels allows the *in situ* control of the liquid flow, which is required for the fabrication of microfluidics device components. A total

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*Corresponding author. Tel.: +39 0223993041; fax: +39 0223993180.
E-mail address: pierangelo.metrangolo@polimi.it (P. Metrangolo)
URL: http://nfmlab.chem.polimi.it
**Corresponding author. Tel.: +39 0223993032; fax: +39 02 23993180.
E-mail addresses: giuseppe.resnati@polimi.it (G. Resnati)
URL: http://nfmlab.chem.polimi.it
***Corresponding author. Tel.: +39 0832 298216; fax: +39 0832 298238.
E-mail addresses: giuseppe.resnati@polimi.it (G. Resnati)
URL: http://nfmlab.chem.polimi.it

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Table 1
Material properties at room temperature

	Molecular weight (amu)	Viscosity (cSt)	Boiling point (°C)	Dielectric strength (kV)	Density (g/cm^3)	Surface tension (dyn/cm)	Polydispersity (Mw/Mn)
Galden SV90	460	0.75	92	34	1.69	16	
Fomblin Z-DOL 2000	2000	85			1.81	24	1.5
NOA72	<1000	0.16		456		38	

integration of the peripheral functions onto single microchips can be possible only when a great variety of chemical and biological processes can be implemented, including technologies for novel microfluidic components integrating more than one function. These functions could be filtering, preconcentration, separation, sorting, mixing, reactants confinement, local chemistry and flow control. The role of the mentioned fluoropolymers in the development of such components can be of interest especially for miniaturized systems, whose typical dimensions are at sub-millimetre scale and thus are characterized by high values of surface-to-volume ratio (S/V). In such geometrically confined systems, also well known as high S/V systems, the driving motion is strongly influenced by surface interactions and localization phenomena, which dominate over the bulk dynamics and usually indicate a fast diffusion regime.

Therefore, the analysis of the dynamical properties of different liquids in confined systems is thus proposed, considering the time condition for a fast diffusion regime as $T_S \gg T_D$. T_S is the surface time, namely the average time of each molecule's interaction with the surface $T_S \cong \rho^{-1}(V/S)$, with ρ related to the molecular relaxation rate near the surface [4] and T_D is the molecular diffusion time according to the Einstein equation $T_D \cong D^{-1}(V/S)$ [5]. In this work, we report an *in situ* and *real-time* microfluidic technique as a direct tool for the analysis of the most relevant properties of fluorine-based liquids in a confined system during the operational regime. For this purpose, we have used as fluidic confined structure a network of microchannels with a rectangular cross-sectional area (Fig. 1), obtained by the conformal contact of a PDMS microstructured mould, fabricated by a soft-lithography technique, and a flat SiO_2/Si substrate.

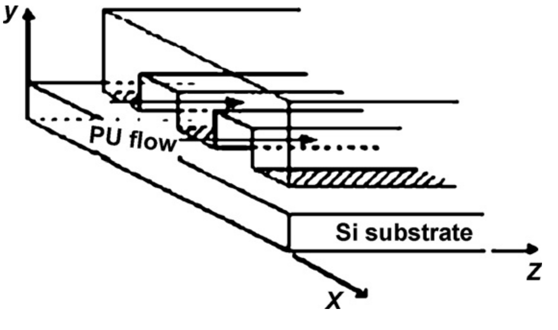

Fig. 1. Schematic of the MIMIC process (features not in scale). The conformal contact between the Si support and a PDMS mould induces the PU to flow inside the micro-channels.

2. Results and discussion

Our microfluidic research bases the capillary condition as the macroscopic motion of a fluid system under the influence of its own surface and interfacial forces, and results from two opposing forces: the liquid adhesion and the cohesive surface tension.

In general, in the absence of other external forces, capillary flow is controlled by the interplay of the various interfacial tensions, the geometry of the solid–liquid–vapour interface and the geometry of the solid interface. For the analysis of our microfluidic system, we choose to focus the attention on the energetic conditions, such as surface tension and contact angle, both of the liquid and the solid interface and the channels geometry. Besides, we assume to neglect the effect of the geometry at the solid–liquid–vapour interface because we have kept constant the experimental contour conditions.

In a horizontal capillary environment (Fig. 1), the fluid driving motion is generally governed by the Laplace equation for the capillary pressure drop [4–6]. Capillary forces provide an alternative means to create a pressure difference in different regions of small hydraulically connected conducts, where the direction of the resulting flow allows the pressure difference to be decreased. Recent literature has demonstrated that the Laplace equation is valid up to nanometre length scale, and that on this scale the filling of nanochannels by capillarity is dominated by the wetting properties of the channel walls [7].

Differences of the meniscus shape during the displacement of the polyurethane, NOA72, and FOMBLIN Z-DOL are well evidenced in Fig. 2a and b. In particular, the dynamic behaviour of NOA72 (Fig. 2a) is characterized by a certain hydrophilic behaviour with a contact angle of $\theta = 80^\circ$, whereas the concave front of the fluorinated liquid (Fig. 2b) reveals a hydrophobic behaviour with a contact angle of $\theta = 120^\circ$.

In a horizontal capillary environment (as the one sketched in Fig. 1) the fluid driving motion is generally influenced both by the interfacial mechanical tension and by the curvature of the different phases, as can be clearly expressed by the Laplace equation for the capillary pressure drop $\Delta p = (2\gamma_{LV}\cos\theta)/r$, where γ_{LV} is the free energy at the liquid–vapour interface and θ is the wetting angle between the liquid and the capillary surface. The Laplace pressure Δp is the pressure difference in the two phases forming the interface, required to sustain the curvature resulting from the surface tension, and represents the thermodynamic conditions that favour the filling process. For a curved interface p is defined as the internal front pressure minus the external front pressure ($\Delta p = \Delta p_{int} - \Delta p_{ext}$). Therefore, evidence of significant negative pressure can be attributed to the