Rheological Behavior of Fugitive Organic Inks for Direct-Write Assembly

Daniel Therriault*[1], Scott R. White[2] and Jennifer A. Lewis[3]

[1] Mechanical Engineering Department, Center for Applied Research on Polymers and Composites (CREPEC), École Polytechnique de Montréal, Montréal, Québec H3C 3A7,Canada

[2] Beckman Institute for Advanced Science and Technology, Autonomic Materials Systems Group, Aerospace Engineering, University of Illinois at Urbana-Champaign, 306 Talbot Lab, 104 S. Wright St., Urbana, IL 61801, USA

[3] Materials Science and Engineering Department, Frederick Seitz Materials Research Laboratory, NSF Center for Directed Assembly of Nanostructures, University of Illinois at Urbana-Champaign, 212d Ceramics Bldg., 1304 W. Green St., Urbana, IL 61801, USA

*E-mail: daniel.therriault@polymtl.ca
Fax: x1.514.340.4176

Received: 21.7.2006, Final version: 15.9.2006

Abstract:
The rheological behavior of a fugitive organic ink tailored for direct-write assembly of 3D microfluidic devices is investigated. Rheological experiments are carried out to probe the shear storage and loss moduli as well as the complex viscosity as a function of varying temperature, frequency and stress amplitude. Master curves of these functions are assembled using time-temperature superposition. The fugitive ink, comprised of two organic phases, possesses an equilibrium shear elastic modulus nearly two orders of magnitude higher than that of a commercial reference ink at room temperature and a peak in the relaxation spectrum nearly six orders of magnitude longer in time scale. The self-supporting nature of extruded ink filaments is characterized by direct video imaging. Comparison of the experimentally observed behavior to numerical predictions based on Euler-Bernoulli viscoelastic beam analysis yield excellent agreement for slender filaments.

Zusammenfassung:
Das rheologische Verhalten einer flüchtigen organischen Tinte für die Herstellung dreidimensionaler mikro-strömungstechnischer Apparate mittels Direkt-Schreibens wurde untersucht. Über rheologische Messungen wurden Speicher- und Verlustmodul sowie die komplexe Viskosität als Funktion verschiedener Temperaturen, Frequenzen und Schubspannungsamplituden bestimmt. Die Masterkurven für diese Funktionen wurden mit Hilfe der Zeit-Temperatur-Superposition zusammengestellt. Die flüchtige Tinte, die ein Gemisch zweier organischer Komponenten ist, weist bei Raumtemperatur ein um ungefähr zwei Dekaden größeres Gleichgewichtsspeichermodul als das einer kommerziell erworbenen Referenztinte auf und das Maximum des Relaxationsspektrums ist um sechs Dekaden länger in der Zeit. Die selbsttragende Natur extrudierter Tintenfäden wurde mittels digitaler Bildanalyse charakterisiert. Die experimentellen Beobachtungen stimmen mit numerischen Berechnungen nach dem viskoelastischen Balkenmodell von Euler-Bernoulli für dünne Stränge sehr gut überein.

Résumé:
Le comportement rhéologique d'une encre fugitive organique utilisée pour l'écriture directe d'appareils microfluidiques tridimensionnels est étudié. Des expériences rhéologiques ont été réalisées pour quantifier les modules élastique et de perte en cisaillement ainsi que la viscosité complexe de l'encre en fonction de différentes températures, fréquences et amplitudes de contrainte. Les courbes maîtresses de ces fonctions ont été assemblées à l'aide de la superposition temps-température. L'encre fugitive, mélange de deux composants organiques, possède à température ambiante un module élastique de cisaillement à l'équilibre environ deux décades supérieur de celui d'une encre commerciale utilisée comme référence et le sommet de son spectre de relaxation est six décades plus long dans le temps. Le comportement auto-supporteur de filaments d'encres extrudés a été caractérisé par l'analyse d'images numérisées. La comparaison entre les résultats expérimentaux observés et les prédictions numériques obtenues à l'aide d'un modèle de poutre viscoélastique Euler-Bernoulli donne un excellent accord pour un filament élancé.

Key words: Direct-write, viscoelastic material, organic ink, structural behavior, microfabrication

This is an extract of the complete reprint-pdf, available at the Applied Rheology website
http://www.appliedrheology.org

cross-section occurs at the support, consistent with the structural behaviour of simply supported beams.

The mid-span deflection measurements are normalized by the filament diameter and shown alongside the corresponding normalized structural model predictions for the fugitive organic ink in Figure 11a. For the range of aspect ratios investigated, the model predictions are slightly lower than the experimental data for extended time periods where the maximum observed deviation was ~ 10% after 1 h for the case $L/d = 10.7$. At short times (i.e. $t < 10$ s) only the predictions for the highest aspect ratio case (i.e. $L/d = 26.1$) exceed the measured values since the predicted deflection rate is quite high. For further insight into the spanning behavior of an ink filament, the mid-span deflection $w(t)$ was normalized so that geometric and material effects are isolated such that,

$$\frac{w(t)d^2}{L^4} = KD(t) \tag{9}$$

and K is a constant. Thus, the model predictions for the three aspect ratios investigated collapse onto a single curve since the material property $D(t)$ is assumed identical. The normalized experimental data are shown in Figure 11b together with the model prediction. In this case excellent correlation is obtained for the slender beam ($L/d = 26.1$) although significant deviations at long times are observed for the short beam cases. The deviation between the experimental data and the model predictions for $L/d = 10.7$ and 14.8 is likely a result of structural model limitations. First and foremost, the quasi-static solution of the Euler-Bernoulli beam theory is not recommended for short beams ($L/d < 20$) since the additional deformation due to the transverse shear is not considered. Additionally, material properties were obtained by rheological experiments under low amplitude shear and are restricted to the linear viscoelastic regime. However, within the nozzle, the ink yields under high shear in the region near the wall ($\tau > \tau_y^{app}$) leading to a sharp decrease in the material stiffness followed by a period of recovery as the ink exits the nozzle. The deformation occurring during the yielding and recovery periods at short times were difficult to observe due to the spatial and time resolutions of the experimental setup used. Other contributing factors such as slumping of the ink cross-section [18] and axial tension in the self-supporting filament [19] may limit the model's application. Developing a more complex structural model without these limitations and numerical simulations by finite element method are expected to provide more accurate deformation predictions at extended time periods for a wider range of filament aspect ratios.

5 CONCLUSIONS

A fugitive organic ink has been developed that shows superior rheological properties compared to a commercial ink used in the direct-write assembly of microvascular networks. A blend of 60wt% low molecular weight paraffin wax and 40wt% high molecular weight microcrystalline wax yields an ink system that extrudes easily at room temperature yet retains structural shape post-deposition. The new organic ink has higher stiffness (about one order of magnitude) across the entire spectrum of applied frequency together with a relatively modest apparent yield stress (1.0 kPa). More importantly, the new organic ink displays a relaxation spectrum centered at 1 s, a shift of 6 decades longer in time compared to the commercial ink. Thus, network structures deposited using the new organic ink are much more stable and persistent. For example, for an aspect ratio (L/d) of 14.8 the total deflection after one hour is less than 20% of the filament diameter for the organic ink compared to about 65% for the commercial ink system. A structural model using Euler-Bernoulli viscoelastic beam mechanics provides good predictive capability for slender ($L/d > 20$) beams and reasonable correlation for filaments with moderate length ($10 < L/d < 20$). Further refinements in process modeling are needed to characterize the ink flow inside the deposition nozzle and the structural recovery immediately after deposition. These analyses will provide important information for the design of future fugitive inks and help define the processing parameters. High-performance inks combined with accurate process modeling of the direct-write assembly technique will enable the creation of microvascular networks with unparalleled complexity and commercialization of technological applications in biomedical, advanced materials and microfluidics.

This is an extract of the complete reprint-pdf, available at the Applied Rheology website
http://www.appliedrheology.org

ACKNOWLEDGMENTS

The authors acknowledge funding for this project provided by AFOSR Aerospace and Materials Science Directorate (Grant # F49620-03-1-0179), U.S. Department of Energy, Division of Materials Science under Award# DEFG02-91ER45439 through the Frederick Seitz Materials Research Laboratory (UIUC), and the NSF Center for Directed Assembly of Nanostructures (Grant # DMR-01-177792). The robotic deposition apparatus used in this work was designed and built by J. Cesarano and the customized software for the 3D fabrication was developed by J.E. Smay. Partial support for D. Therriault was provided by the University of Illinois Nanoscience and Technology Center Fellowship and the government of Québec (NATEQ).

REFERENCES

[1] Ziaie B et al.: Hard and Soft Micromachining for BioMEMS: Review of Techniques and Examples of Applications in Microfluidics and Drug Delivery, Adv. Drug Delivery Rev. 56 (2004) 145-172.
[2] Losey MW et al.: Microfabricated Multiphase Packed-Bed Reactors: Characterization of Mass Transfer and Reactions, Ind. Eng. Chem. Res. 40 (2001) 2555-2562.
[3] Walker GM et al.: Cell Infection within a Microfluidic Device using Virus Gradients, Sens. Actuators B 98 (2004) 347-355.
[4] White S et al.: Autonomic Healing of Polymer Composites, Nature 409 (2001) 794-797.
[5] Therriault D et al.: Chaotic Mixing in Three-Dimensional Microvascular Networks Fabricated by Direct-Write Assembly, Nature Mater. 2 (2003) 265-271.
[6] Lewis JA, Gratson GM: Direct Writing in Three Dimensions, Mater. Today 7 (2004) 32-39.
[7] Therriault D et al.: Fugitive Inks for Direct-Write Assembly of Three-Dimensional Microvascular Networks, Adv. Mater. 17 (2005) 395-399.
[8] Cesarano J et al.: Robocasting Provides Moldless Fabrication from Slurry Deposition, Ceram. Ind. 148 (1998) 94-102.
[9] Ward IM, Hadley DW: An Introduction to the Mechanical Properties of Solid Polymers, J. Wiley and Sons, New York (1993).
[10] Wunderlich B: Thermal analysis, Academic Press Inc., New York (1990).
[11] Rueb CJ, Zukoski CF: Viscoelastic Properties of Colloidal Gels, J. Rheol. 41 (1997) 197-218.
[12] Therrriault D: Ph.D. dissertation, Department of Aerospace Engineering, University of Illinois at Urbana-Champaign (2003).
[13] Carreau PJ et al.: Rheology of Polymeric Systems, Principles and Applications, Hanser, Cincinnati (1997).
[14] Vega JF et al.: Model Linear Metallocene-Catalyzed Polyolefins: Melt Rheological Behavior and Molecular Dynamics, J. Rheol. 47 (2003) 1505-1521.
[15] Polacco G et al.: Dynamic Master Curves of Polymer Modified Asphalt from Three Different Geometries, Appl. Rheol. 13 (2000) 118-124.
[16] Ferry JD: Viscoelastic Properties of Polymers, J. Wiley and Sons, New York (1980).
[17] Chen TM: The Hybrid Laplace Transform/Finite Element Method Applied to the Quasi-Static and Dynamic Analysis of Viscoelastic Timoshenko Beams, Int. J. Numer. Methods Eng. 38 (1995) 509-522.
[18] Smay JE et al.: Colloidal Inks for Directed Assembly of 3-D Periodic Structures, Langmuir 18 (2002) 5429-5437.
[19] Morissette SL et al.: Solid Freeform Fabrication of Aqueous Alumina-Poly(vinyl alcohol, J. Am. Ceram. Soc. 83 (2000) 2409-2417.

This is an extract of the complete reprint-pdf, available at the Applied Rheology website
http://www.appliedrheology.org