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Parallel high-throughput microanalysis of materials using microfabricated full bridge device arrays

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An array of microfabricated full bridge devices has been implemented for the rapid thermal microanalysis of polymers. In each microelectromechanical system device, four strain gauges were formed in silicon cantilevered microbeams and were configured as a Wheatstone bridge circuit. Glass transition temperatures T_g were measured by the quantitation of the strain produced in the sensor by the stress applied by a polymer layer to the cantilevered microbeams. The measured strain was analyzed as a function of chip temperature for the change in the slope, which was indicative to T_g . Resolution of T_g determinations of amorphous and crystalline polymers was $<0.25^\circ\text{C}$ and $<2.0^\circ\text{C}$, respectively, being attractive for combinatorial screening of polymers. Our approach is a practical alternative to known methods for T_g determinations because of the immunity to the variations in the amount of deposited material and its viscosity, vapor pressure of employed solvent, and ease of multiplexing into dense sensor arrays. © 2004 American Institute of Physics.
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Thermal behavior in polymers is of considerable technological importance. Knowledge of thermal transitions is essential at the stages of material formulation, performance testing, and end-use.¹ Polymers for practical applications are typically formulated from multiple components to improve their physical and chemical properties.² These formulation advances often affect the large-scale cooperative movement of polymer chain segments and thus the glass transition temperature T_g . In general, predictions of T_g in polymers of different composition, processing, and end-use conditions are difficult based on existing knowledge. Rapid screening of a variety of polymeric and other types of materials can be achieved using combinatorial methods³ where parallel reactions are coupled with the robotic sample handling and high-throughput (HT) materials characterization. Data from combinatorial and HT experiments, coupled with data-mining methods, can be a very effective tool to generate knowledge.⁴ We are developing sensor^{5–7} and spectroscopic^{8–10} techniques because the success of combinatorial and HT methodologies strongly relies on analytical tools with improved capabilities.⁴

In this letter, we implement microfabricated full bridge devices for HT determinations of T_g for multiple polymers simultaneously. Earlier, thermodynamic transitions of materials were determined using acoustic-wave devices,¹¹ ultrasonic transducers,¹² microhotplates,¹³ micromechanical calorimetric sensors,¹⁴ and fluorescence polarization sensors.¹⁵ For combinatorial screening, it is useful to integrate a transducer array into an automated “combinatorial cycle.”¹⁶ Unfortunately, reported transducer configurations have certain limitations for combinatorial screening. They often suffer from the uncertainty in sample volume delivered to the transducer due to the decreased precision of robotic dispensing of solutions of elevated viscosity (>100 cp), of solvents with

high vapor pressure (>200 Torr), and of small volumes (<5 μL). These factors result in significant variations in transducer response. For example, an increase in mass of deposited material onto a quartz crystal resonator or a surface-acoustic wave device stops an oscillation due to high damping.¹¹ Performance of the embedded heaters in micro-machined calorimeters is affected by the nature and amount of deposited material.¹³ Serial, rather than parallel, operation of sensors in an array for materials screening is too slow.¹⁷

We have developed a sensor array system that is free from these limitations. We measure the viscoelastic properties of polymers under variable temperature using an array of microelectromechanical system (MEMS) strain gauge devices manufactured at Hygrometrix, Inc. (Alpine, CA) and further relate these measurements to T_g . Each device has four strain gauges which are used in individual arms of a full bridge [Fig. 1(a)]. The full bridge structures were micromachined as described previously¹⁸ with each arm of the bridge being a cantilever microbeam that contained an embedded semiconductor strain gauge. The four embedded strain gauges were configured as a Wheatstone bridge circuit directly on the sensor chip [see Fig. 1(b)] and employed the piezoresistive effect to measure beam stress.¹⁸ In contrast to conventional glued-on metal foil strain gauges, these piezoresistive strain gauges exhibited no mechanical defects from overload.¹⁸ This brought an important operational capability to our sensors. An embedded on-chip thermistor added another important operational capability to the sensor in providing independent temperature-monitoring ability for individual sensors.

T_g measurements with the sensor were done by quantitation of the strain produced in a sensor substrate by the stress applied by a polymer layer to the cantilevered microbeam. During a thermal sweep, a polymer film experiences a bulk dimensional change. This polymer behavior is explained by the free volume model of glass transition,¹ which

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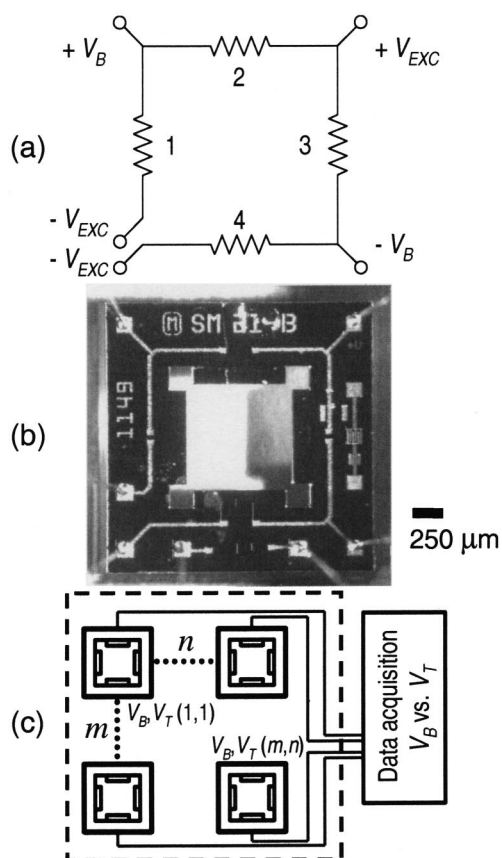


FIG. 1. Micromachined full bridge device configuration for high-throughput thermal analysis of polymers. (a) Electrical schematic, 1–4, strain gauges, (b) general view, and (c), layout of device array.

considers the free volume V_f of a substance as the difference between its specific volume V and the space actually occupied by the molecules V_0 , $V_0 = V' + a_g T$, where V' is the extrapolated volume of the material at $T = 0$ K and a_g is its thermal expansion coefficient. During the thermal cycling of the sensor, the film undergoes a displacement parallel and normal to the adjacent microbeam surfaces, however, with the exception of the film surface that is in contact to the cantilever beam. This behavior produces shear stresses at the film-beam interface that causes the cantilever beams to deflect. The deflection is measured as a resistance change in the embedded strain gauges, and is proportional to the shear stress. Consequently, the polymer viscoelastic change is transduced into a proportional differential voltage change in the bridge circuit.

Our system for parallel thermal microanalysis of polymers comprised of an array of four MEMS sensors but can be easily extended to a $m \times n$ array [Fig. 1(c)]. A simultaneous and continuous response from each device was achieved using a data acquisition program written in LabVIEW (National Instruments, Austin, TX). Each MEMS sensor was driven by applying a stable excitation voltage V_{EXC} and provided a direct 0–5 VDC voltage output V_B [cf. Fig. 1(a)]. The voltage output V_T was also provided for temperature measurement from the on-chip thermistor. The measured relation V_B vs V_T was further analyzed for the change in the slope, which was indicative to the thermal transition in the polymer. The analog outputs from the sensors provide an advantage for combinatorial screening by means of a

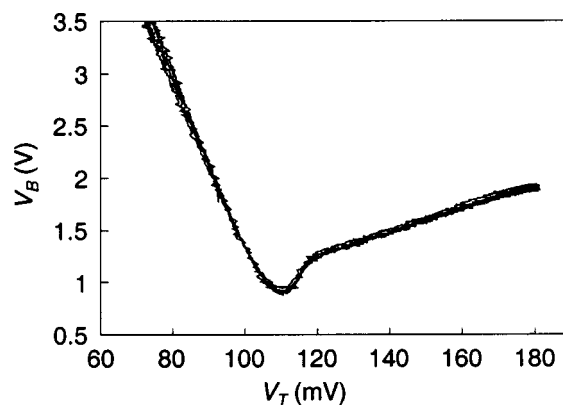


FIG. 2. Reproducibility of device performance upon multiple ($n=4$) heating cycles of a poly (methylmethacrylate) film.

straightforward multiplexing of sensors with parallel high-speed data acquisition. Importantly, parallel analysis not only speeds up the measurement process of multiple samples, but also eliminates variation sources that otherwise contribute to random errors in serial analysis.¹⁶

Performance reproducibility was evaluated by repetitive thermal cycling of a variety of polymers deposited onto the sensors. Polymers were applied onto the sensors by dissolving polymers in chloroform and delivering a small amount of solution (5–10 μ L) onto the devices using a multichannel automatic pipetting system. After solvent evaporation, the sensor array was positioned into a temperature-controlled chamber. Temperature of the chamber was ramped at a 10 $^{\circ}$ C/min rate in the range from 30 to 180 $^{\circ}$ C in air. Temperature control of heating/cooling cycles was <0.1 $^{\circ}$ C. Figure 2 depicts typical thermal traces from one of our sensors upon multiple ($n=4$) heating cycles of a polymer film. Importantly, as shown in this figure, the repetitive thermal cycles under the selected conditions do not alter T_g .

Dependence of the device response in determination of T_g was evaluated using solutions of different polymers at 0.025–0.25 g/mL concentrations. The response of the MEMS devices was independent on the concentration of polymer used for deposition (see Fig. 3). This desired lack of sensitivity to the amount of the deposited polymer is provided by the nature of the piezoresistive strain gauge which exhibits no mechanical defects from overload.¹⁸ Such behavior is important in reducing sensor errors due to the variability

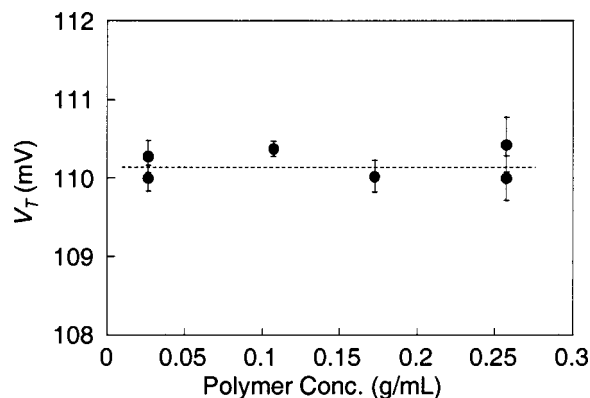


FIG. 3. Typical insensitivity of device response in determination of T_g to changing mass of deposited poly(methylmethacrylate) polymer.

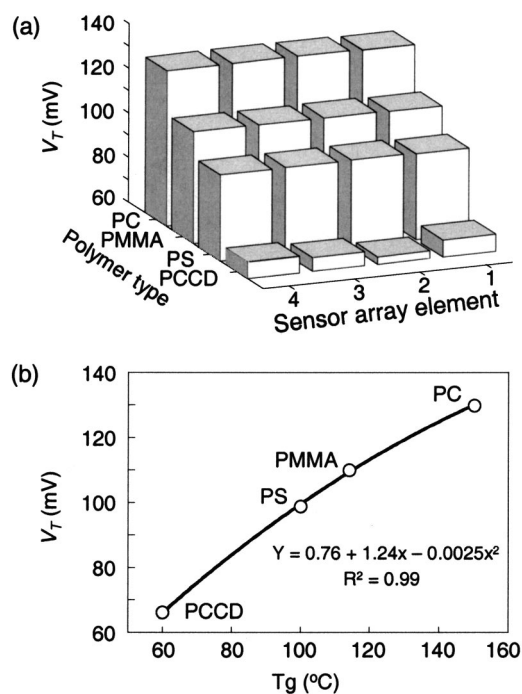


FIG. 4. Performance of MEMS device array for parallel determination of T_g . (a) Reproducibility of device array performance. (b) Calibration results for determination of T_g of different polymers.

ity in materials synthesis, polymer dissolution, and robotic delivery.

Results of determination of T_g of multiple polymers using our MEMS sensor array are presented in Fig. 4(a). This figure illustrates good reproducibility of analysis of amorphous polymers such as polycarbonate (PC), poly(methylmethacrylate) (PMMA), and polystyrene (PS). A typical standard deviation of T_g determinations for amorphous polymers was $0.15\text{--}0.25^\circ\text{C}$ ($n=4$). A slightly larger variability in T_g determinations of 1.9°C ($n=4$) was observed for poly (1,4-cyclohexylenedimethylene-1,4-cyclohexanedicarboxylate) (PCCD) polymer. This elevated variability was consistent with conventional determinations using differential scanning calorimetry¹ because of the crystalline nature of PCCD. T_g determinations in crystalline polymers can be improved by a thermal annealing step before T_g measurement. The relation between the response of thermistors V_T of each of the sensors in the array and reference T_g values for these polymers is presented in Fig. 4(b).

In conclusion, our developed MEMS sensor array can be applicable for the evaluation of thermal transitions in polymers, shape-memory alloys, nucleic acids, and other materials systems. Applications of these sensors can be not only for combinatorial screening, but also for process analysis.¹⁹ The operation of the developed sensors in parallel in the array not only provides a well-recognized acceleration in the screening rate, but also considerably reduces or even eliminates variation sources, which randomly affect sensors response during the one-at-a-time analysis.

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