Guide to NIST Instrument for the Measurement of Curing Kinetics (Degree of Conversion), Polymerization Shrinkage Stress, and Temperature for Photopolymerized Materials

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Simultaneous Measurement of Degree of Conversion, Polymerization Shrinkage Stress, and Exotherm Temperature for Photopolymerized Materials Using NIST-developed Instrument

Introduction

Photopolymerized materials are widely used in applications ranging from electrical and optical materials, structural materials, coatings and adhesives, to various biomedical applications such as dental restoration. Polymerization shrinkage, *i.e.* the volume a material decreases as monomers convert to polymers during solidification, is a common feature for radical-photopolymerized materials. Associated with the shrinkage, undesired polymerization shrinkage stress (PS) is inevitably developed due to the confinement of shrinkage in practical applications. In dental restorations, photopolymerized composites as restorative materials are confined by the cavity walls, the result of which could cause considerable PS development at the restorative-tooth interface during and after polymerization thereby imparting material failure and tooth decay from subsequent bacterial biofilm ingrowth. To better understand and control the PS behavior during photopolymerization, a technique that can accurately monitor the development of PS is required.

One of the common features in photopolymerization processes is that gelation can take place very rapidly, *e.g.* in less than a second under a high-intensity irradiation condition. Therefore, it is important to accurately follow the curing kinetics (normally characterized by the degree of monomer-polymer conversion, DC) of such fast reactions for a better assessment of the performance of monomers, as well as understanding and controlling the curing process. To understand the development of PS in association with the reaction kinetics, it is necessary to measure these properties simultaneously. It is known that slight changes in sample configuration, irradiation conditions, or instrumental compliance can greatly affect the mechanical properties of complex photopolymerizable systems. Hence, there is a strong desire to simultaneously measure PS and DC for the same sample.

Free radical photopolymerizations are generally exothermic reactions. Since temperature rise during photopolymerization is considered a critical parameter in determining the applicability of the material (*e.g.* in dental restorations), and reaction exotherm is also associated with the curing kinetics, simultaneous measurement of exothermic temperature for the same sample is also desired.

To resolve these measurement needs, an instrument developed at NIST (Figure 1, called polymerization stress tensometer) is capable of providing simultaneous and real-time measurement of polymerization shrinkage stress, degree of conversion, and exothermic temperature of a sample during a photopolymerization process. Figure 2 shows the tensometer’s graphical user interface (GUI) displaying the measured data collected during a photopolymerization experiment using the instrument.
Figure 1. Images of NIST-developed instrument for simultaneous measurement of polymerization stress, degree of conversion, and exothermic temperature from (A) overall view, and (B) close-up view of the sample mounting region.
Figure 2. NIST tensometer data acquisition shown, demonstrating an example of the curing light switched on at 20 seconds and off at 60 seconds.

**Instrument components and software installation**

The NIST tensometer (Figure 1) is a cantilever-beam based instrument. To provide the simultaneous measurement of PS, DC, and exothermic temperature, as well as control of curing light, certain commercial off-the-shelf (COTS) devices are integrated into the tensometer system. The devices, shown in Figure 3, include:

- Capacitive displacement sensor driver with probe (CPL 190, Lion Precision) for detecting beam deflection of the tensometer (Figure 3B).
- Data acquisition (DAQ) device (USB-2404-10, Measurement Computing Corp. [MCC]) for converting analog signal to computer-readable digital data (Figure 3C).
- Curing light system with controller (6340 ComboSource, Arroyo Instruments) and light emitting diode (LED LZ1-10DB00, LED Engin) (Figure 3D). The curing light shown here is a single blue color LED, which emits a spectrum with a concentrated peak centered near 465 nm, as shown in Figure 4. This spectrum matches well with the absorption spectrum of a camphorquinone (CQ)/amine system, the typical photo-initiator used for dental materials. For an initiator system other than CQ/amine, the LED bulb can easily be replaced with a bulb of a different emission spectrum (e.g. ultraviolet (UV) range).
- Thermocouple-to-analog converter (TAC80B-T, Omega Electronics) with twisted pair thermocouple probe (Type-T IT23, Physitemp) and connector (SMPW-T-MF, Type-T, Omega) (Figure 3F).
- (Optional) Near infrared (NIR) spectrometer (NIRQuest512-2.2, Ocean Optics) and infrared (IR) light source (HL-2000, Ocean Optics) for spectra monitoring (Figure 3A).
- (Optional) USB-controlled power strip (PowerUSB-Basic, PowerUSB), to power on/off a user-supplied curing light, if applicable (Figure 3E).

Figure 3. Devices integrated with NIST tensometer system. (A) NIR spectrometer [left] and IR light source [right]; (B) Driver of displacement sensor; (C) DAQ device; (D) Curing light system [right] and its controller [left]; (E) USB-controlled power strip; (F) Thermocouple-to-analog converter with connector and thermocouple wire.

Figure 4. Spectrum of the blue curing light for CQ/amine-based materials measured using a spectrometer.
Data collection and control of irradiation for the NIST tensometer system are realized using a custom LabVIEW-based (National Instruments) graphical user interface. Therefore, in order to run an experiment using the NIST tensometer system, the LabVIEW 2014 (32-bit) engine, the device drivers and the executable version of the graphical user interface program, also called as Tensometer program, need to be installed on the user’s data acquisition computer beforehand. All the COTS devices (Figure 3) are connected to the computer through universal serial bus (USB) ports and the LabVIEW drivers for these devices are available on the compact disks (CDs) supplied with the device by the original equipment manufacturer (OEM). Please refer to the manufacturer-provided user manual of each device for the setup and specific device driver installation. With the OEM CDs, a USB drive with the Tensometer program which needs to be copied on the user’s computer is provided. Briefly the installation procedure can be summarized as below:

1) In the provided USB drive, under the ‘Run-Time Engine’ folder, one will find a setup labelled ‘LabView engine’, which needs to be installed. Secondly, install the setup file under the ‘NI-VISA Runtime’ folder. Lastly, copy the folder ‘Tensometer_v2016’ on to the computer.

2) Install the setup files for the MCC DAQ, the Arroyo Instruments and the powerUSB by using the appropriate OEM CD provided.

3) The OceanView software can be optionally be installed by selecting the appropriate (32-bit or 64-bit) installation file under the Ocean optics folder from the USB drive. It can also be alternatively downloaded from ‘www.oceanoptics.com/oceanview-downloads’. Lastly, install the OmnidriverSPAM installer provided in the USB drive under the same folder.

There are several checks that are necessary before one can start using the Tensometer program. The first step involves opening the InstaCal program on the computer which was installed through the MCC DAQ CD.
Figure 5. Screenshot of the InstaCal software showing successful communication with the DAQ device

After clicking the icon, highlighted in red, a test board appears to check the output of the displacement sensor and the temperature sensor which can be connected through the four available channels on the DAQ device (Ch0, Ch1, Ch2 and Ch3). A good visual check would be to gently tap on the cantilever beam and check the corresponding variation in the voltage (in the appropriate channel) in the right window of Figure 5. The second step would involve checking communication with the arroyo instrument controller by opening the Arroyo control software installed previously. Attempt connecting to the controller by selecting the USB serial port option as shown in Figure 6. An example of a successful connection is shown in Figure 6. The third and final check would be to use the OceanView software to check the spectrum being recorded from the NIR spectrometer.

Figure 6. Screen shot of the Arroyo instruments software showing successful communication with the controller.

Testing mechanics

A simple schematic for the tensometer is shown in Figure 7A. Using this instrument, an uncured disk-shaped specimen is bonded to two flat, vertical quartz rods (see Appendix for the manufacturer information) that have been polished and silanized to promote adhesion between the specimen and rods. The rods are polished with 320/P400 grit sandpaper with water as a lubricant. The upper rod clamped to the steel cantilever beam using the upper collet holder and the lower rod fixed on the tensometer base stand using the lower collet holder. A non-tacky Teflon sleeve (see Appendix) with two holes (an injection hole and a smaller air-venting hole) is used to encase the specimen between the upper and lower quartz rods in the tensometer. As curing light transmits
through the lower rod onto the specimen, polymerization shrinkage induces a deflection in the beam (Figure 7B), which is continuously recorded by a displacement sensor assembled at the free end of the beam. The PS is then calculated in LabVIEW through the beam formula:

Equation (1):  \[ \sigma = \frac{F}{A} = \frac{\delta E I}{\pi r^2 \left( \frac{a^2 (3l-a)}{6} + \frac{h^2 l (1+\nu)}{4} \right)} \]

where \( \sigma \) is the PS and \( F \) is the force exerted by the sample shrinkage; \( A \) and \( r \) are the cross-sectional area and the radius of the sample, respectively; \( \delta \) is the beam deflection at the free end; \( E \) = 203 GPa and \( I = wh^3/12 \) are the Young’s modulus for stainless steel and the moment of inertia of the beam cross-section, respectively; \( h \) and \( w \) are the height and width of the beam cross-section in mm, respectively; \( \nu \) (= 0.305) is the Poisson’s ratio of the beam material; \( l \) is the length of the beam in cm, as measured from the ‘0 cm’ marking to the metal target (shown in Figure 1A), and \( a \) is the distance between the sample position and the clamped edge of the beam.

Of the two terms present in the denominator of Equation (1), one can note that the first term represents the bending contribution, while the second term represents shearing. The second term becomes negligible as the ratio of \( a/h \) increases which is the case for most positions on the cantilever beam instrument. Hence, a simplified equation of the PS is,

Equation (2):  \[ \sigma = \frac{F}{A} = \frac{\delta E I}{\pi r^2 \left( \frac{a^2 (3l-a)}{6} \right)} \]

Figure 7. (A) Schematic diagram of the instrument for simultaneous measurement of polymerization stress and curing kinetics (with temperature measurement not shown). (B) Schematic of the cantilever beam configuration for polymerization stress measurement.

The NIR data acquisition is realized by configuring two optical-fiber cables (preferably 1 mm fiber diameter) onto the sides of the sample (Figure 1B), with one cable connected to the IR light source and the other to the NIR spectrometer (Figure 3A). By doing so, the spectra of the sample are monitored continuously during transmission. For the calculation of DC in LabVIEW, the area under the absorption peak of the methacrylate functional group (for typical dental materials) centered at 6165 cm\(^{-1}\) (C=\(\text{C-H}\) stretching, first overtone) is used (Figure 8). The area
under this peak is determined by subtracting a linear baseline across the edges of the peak for each spectrum obtained. Small variations in the intensity of the baseline are compensated for since the peak area is always calculated relative to the baseline of each individual spectrum. The DC is calculated by taking the peak area of the sample prior to the start of irradiation (Area\text{monomer}) and at each time point during the photopolymerization process (Area\text{polymer}) based on the following formula:

Equation (3): \( DC(\%) = (1 - \frac{\text{Area}_{\text{polymer}}}{\text{Area}_{\text{monomer}}}) \times 100 \)

**Figure 8.** Typical spectra of methacrylate materials before and after photopolymerization. Absorption peaks associated with the methacrylate =CH\text{2} bonds (first overtone) are highlighted by the asterisk at 6165 cm\textsuperscript{-1}.

Temperature of the sample during the photopolymerization process is measured using a microprobe thermocouple (Physitemp Instruments) inserted into the center of the specimen (Figure 9) through the injection hole in the Teflon sleeve. Due to the small size of the probe, the insertion of the probe into the sample does not significantly affect the sample integrity or the measurement reliability of PS and DC. Also, the thermocouple can be easily prepared for reuse after each experiment by carefully stripping the wire insulation and twisting the ends together.
During a typical polymerization process, the actual temperature rise is the result of both reaction exotherm and heat generated by light irradiation. Contribution from the later factor can be determined by applying a second irradiation (to the post-cured sample) of the same irradiation conditions as those imposed during initial curing of the sample. Figure 10 shows typical curves of the real-time temperature rises from the total contribution (exotherm plus irradiation), contribution from light irradiation only, and the contribution from the reaction exotherm (difference between total and irradiation). Therefore, the exotherm temperature can be measured by the tensometer system by applying this post-cure irradiation method.

**Calibration**

- Displacement sensor

The displacement sensor used in the tensometer system is a capacitive sensor with 20 nm resolution (per manufacturer specifications). The sensitivity of the sensor was OEM factory-
calibrated as 10 mV/μm, which means a 1 μm change of the displacement between the metal target and the sensor probe (Figure 1A) corresponds to a 10 mV change in the sensor voltage reading. To validate this sensitivity value (used to convert the voltage reading of the sensor to the deflection of the beam for the PS calculation), a self-calibration is performed by using a known weight (P), as shown in Figure 11A. For each hanging location along the beam from the clamped beam edge (a), a sensor voltage reading (ΔV, voltage difference between when there is no weight and when there is a weight on the beam) is recorded from the MCC DAQ InstaCal software (installed from manufacturer-provided CD) and the theoretical beam deflection at the free end (δ) is calculated from the beam formula:

Equation (4): \[ \delta = 2P \frac{a^2(3l-a)}{Ewh^3} \]

where the parameters are the same as those defined in Equation (1). The voltage reading is plotted against the calculated deflection as shown in Figure 11B. Linear fitting (y = mx+b) of the data points provides the actual slope in mV/μm, which is very close to the sensitivity value provided by the manufacturer specifications. The self-calibration value (slope m) is used by the tensometer LabVIEW software. It is recommended that the user perform this calibration whenever the instrument is moved to a new location. Recalibration is also recommended (at regular intervals) to maintain the instrument sensitivity. The new recalibrated value can be entered into the ‘Ports and calibration constants’ excel file, under the ‘Data files’ folder.

![Figure 11. (A) Image of NIST tensometer with deadweight for displacement sensor calibration. (B) Calibration plot of the voltage reading from the displacement sensor vs. the calculated beam deflection. The solid line is a linear fit of the data.](image)

- Curing light

For the curing light system (shown in Figure 3D), the controller uses operating current (in units of mA) to control the output power (in units of mW) of the system. In order to directly control the intensity of curing light (irradiance in units of mW/cm², a typical parameter for curing light in the study of photopolymerization) using the tensometer’s LabVIEW graphical user interface, a
calibration procedure is needed to determine the correlation coefficients between the current (mA) and light intensity (mW/cm²).

The intensity of the curing light is calibrated by using a commercial laser power meter (PowerMax-USB PM2, Coherent Inc.) to measure the intensity at the upper end of the lower rod where the sample is bonded, as shown in Figure 12A. By recording the measured output power for different input current values, a plot of light intensity (power divided by cross-sectional area of the quartz rod) as a function of current can be obtained, as shown in Figure 12B. The correlation between current and intensity is non-linear and a simple polynomial equation \( y = ax^3 + bx^2 + cx \) is used to fit the data. The three fitting coefficients \( a, b \) and \( c \) are used to convert light intensity into current for the tensometer’s LabVIEW program. The light intensity calibration is required whenever a new curing light bulb is installed in the tensometer system or the sample diameter size (quartz rod diameter) is changed. These new coefficients need to be entered in the ‘Ports and calibration constants’ excel file, under the ‘Data files’ folder, in the appropriate row corresponding to the rod diameter in descending order of coefficients \( \text{ax}^3 + \text{bx}^2 + \text{cx} \). Please note that the calibration values provided with the current software are by the assumption that the quartz rods are of diameter 2.5 or 6 mm, 17.1 ± 0.2 cm in length and are polished with 320/P400 grit sand paper. When operating the tensometer, the user should avoid looking directly at the powered light source and laser safety glasses may be worn as a precaution.

**Figure 12.** (A) Image showing the calibration set-up for curing light intensity. (B) Calibration plot of the input current (using 2.5 mm rod) vs. light intensity. The solid red line is a polynomial fit of the data.

**Uncertainty in the NIST Polymerization Stress Tensometer (PST)**

A known weight (\( P \)) at a hanging location along the beam (as shown in Figure 11A) produces a capacitive voltage (\( V \)) reading and a calculated deflection (\( \delta \)), Equation (4). The voltage readings are plotted against the calculated deflections corresponding to various locations of the weight,
Figure 11B. The linear fitting of the data points provides the actual slope \( K \), expressed in Equation (5), unit: mV/μm, used to obtain the polymerization shrinkage stress \( PS \), unit: Pa) during the photocuring process for composite resins:

Equation (5): \( K = \frac{V}{\delta} \)

The expression of relative standard uncertainty in the measurement of \( K \), \( u(K) / K \), is the combined relative standard uncertainties as follows:

Equation (6): \( \frac{u(K)}{K} \approx \sqrt{\left(\frac{u(V)}{V}\right)^2 + \left(\frac{u(\delta)}{\delta}\right)^2} \)

\( u(V) / V \) is the relative standard uncertainty of the capacitive probe. \( u(\delta) / \delta \) is the relative standard uncertainty of the calculated displacement due to the uncertainties in the beam dimensions (length, height, and width of the beam) from machining and the beam elastic modulus, which can be estimated as follows:

Equation (7):

\[
\frac{u(\delta)}{\delta} \approx \sqrt{\left(\frac{u(P)}{P}\right)^2 + \left(\frac{u(w)}{w}\right)^2 + \left(\frac{3u(h)}{h}\right)^2 + \left(\frac{u(l)}{l}\right)^2 + \left(\frac{u(a)}{a}\right)^2 + \left(\frac{3u(a)}{a}\right)^2 + \left(\frac{u(E)}{E}\right)^2}
\]

\( u(P) / P \), \( u(w) / w \), \( u(h) / h \), \( u(l) / l \), \( u(a) / a \), and \( u(E) / E \) are the relative standard uncertainty of the weight used to cause the beam deflection, beam width, beam height, beam length, sample position, and beam elastic modulus (beam material), respectively.

Equation (7) can be simplified as Equation (8) since the \( \frac{u(a)}{a} = \frac{u(l)}{l} \):

Equation (8): \( \frac{u(\delta)}{\delta} \approx \sqrt{\left(\frac{u(P)}{P}\right)^2 + \left(\frac{u(w)}{w}\right)^2 + \left(\frac{u(h)}{h}\right)^2 + 9\left(\frac{u(l)}{l}\right)^2 + 14\left(\frac{u(E)}{E}\right)^2} \)

Finally, the relative standard uncertainty in the measurement of polymerization stress \( PS \) using NIST PST, \( u(PS) / PS \), should be the combined relative standard uncertainties from the measurements of \( K \) and the sample cross-sectional area, \( A \), as follows:
Equation (9):
\[ \frac{u(PS)}{PS} \approx \sqrt{\left( \frac{u(K)}{K} \right)^2 + \left( \frac{u(A)}{A} \right)^2} \]

where \( \frac{u(A)}{A} \) is the relative standard uncertainty of sample cross-sectional area. It is the user’s responsibility to measure the sample cross-sectional area \( A \), and to evaluate the associated relative standard uncertainty, that appear in Equation (9).

Based on the values listed in the Table 1, Eq. 8 gives \( \frac{u(\delta)}{\delta} = 11.18 \times 10^{-4} \). Finally, with \( \frac{u(V)}{V} = 6 \times 10^{-4} \) from the Table 1, Eq. 6 gives \( \frac{u(K)}{K} = 0.1269\% \). Thus, if the \( \frac{u(A)}{A} \geq 1\% \), the relative standard uncertainty of NIST PST (\( \frac{u(PS)}{PS} \)), expressed in Equation (9), can be simplified as:

Equation (10):
\[ \frac{u(PS)}{PS} = \frac{u(A)}{A} \]
Table 1. The relative standard uncertainty for each component of the instrument:

<table>
<thead>
<tr>
<th>Source</th>
<th>Description</th>
<th>Relative Standard Uncertainty</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displacement Sensor</td>
<td>Voltage reading from the capacitive probe (V)</td>
<td>0.06 %</td>
<td>The measurement of the sensor (Lion Precision Corp.) used for displacement is traceable to a length standard maintained by NIST. Detailed traceability information is reported in the calibration report, which conforms to ISO Q10012-2003, and will be delivered with NIST PST.</td>
</tr>
<tr>
<td>Weight</td>
<td>A known weight (P) used in the self-calibration process</td>
<td>0.01 %</td>
<td>Standard weights such as those provided by Troemner LLC can be used by the user. The measurement of weight is traceable to NIST Test Number 822-275872-11 based on ASTM E617 Class 1 tolerances.</td>
</tr>
<tr>
<td>Cantilever Beam</td>
<td>Beam Width</td>
<td>0.01 %</td>
<td>NIST fabricated beam</td>
</tr>
<tr>
<td>Cantilever Beam</td>
<td>Beam Height</td>
<td>0.01 %</td>
<td>NIST fabricated beam</td>
</tr>
<tr>
<td>Cantilever Beam</td>
<td>Beam Length</td>
<td>0.01 %</td>
<td>NIST fabricated beam</td>
</tr>
<tr>
<td>Cantilever Beam</td>
<td>Beam Material (Elastic Modulus)</td>
<td>0.1 %</td>
<td>NIST measurement of elastic modulus</td>
</tr>
</tbody>
</table>

Note: Measurement uncertainty from the physical sample preparation, such as sample cross-sectional area and sample location along the beam, should be minimized according to the practice guide.

**Testing procedures**

1. **Experiment preparation setup**
   
   Several preparation steps are required before one can run an experiment with a dental composite on the NIST tensometer. First, some precautionary steps that need to be taken are:
• Uncured samples are photo-reactive and, hence, tensometer users should protect samples from curing wavelengths by limiting interfering sources of light from the room (e.g. natural light from outdoors, blue or UV light emitted by other devices, overhead fluorescent light fixtures, etc.) prior to running an experiment.
• The NIR instrumentation should be powered on and warmed up for 30 minutes prior to use.
• Quartz rod ends should be polished and silanized prior to running the experiments. The length of the two quartz rods needed for the experiment are around 17 cm (bottom quartz rod) and 5cm (top quartz rod). The length of the bottom quartz rod needs to be precise, however, the suggested value of 5cm for the top quartz rod is a suggestion only and variations in its length will have no impact on the experiment The silanization process is conducted by applying a 1 % by mass acetone solution of 3-methacryloxypropyltrimethoxysilane (MPTMS; Gelest, Morrisville, PA) activated with 0.1 % by mass formic acid to the end of the rods. The silanized rods are then heated in an oven at 60 °C for 1h before use.

After following the necessary precautionary steps, following are the steps required to setup the NIST tensometer for the experiment:

Step 1: Select the desired beam compliance (sample position) and sample size (rod diameter). Beam compliance can be adjusted by varying the sample position along the beam (Figure 13) by sliding the upper collet holder to the desired position and tightening the top-center screw to fix the holder in place. The vertical, etched line on the upper collet holder is used to calculate the sample’s position ($a$) on the beam (relative to the ‘0 cm’ marking). The compliance is calculated by equation:

Equation (5): $C = \frac{a^3}{3EI}$

where $C$ ranges from 0.33 $\mu$m/N to 12.12 $\mu$m/N (for the rigid stainless steel beam) for the sample positions $a = 6$ cm to $a = 20$ cm by applying the same parameters as those defined in Equation (1). Sample size is determined by the diameter of the quartz rods used for bonding with the sample. When rods with a specific diameter are chosen, the corresponding collets and Teflon sleeve that match with the rod’s diameter should also be used. Currently, sample diameters of 2.5 mm and 6 mm are available for this version of the instrument.
**Figure 13.** Preparation for a test using the tensometer.

**Step 2:** Insert the two quartz rods (both with one end silanized to promote adhesion) into the upper and lower collet fixtures, with the silanized rod ends facing toward each other, and gently fasten the rods in place using the upper and lower collets. The upper and lower rod lengths are shown in Figure 13. Slide a Teflon sleeve (with same diameter as rod) onto either one of the two rods (Figure 14A). The recommended Teflon sleeve height will vary based on desired sample size. Teflon sleeve height must be large enough to accommodate the sample height chosen by the user and it is recommended that the sleeve preparation be kept consistent for each set of experiments. Prepared sleeves should slide freely (with minimal friction) along the quartz rods. Care must be taken to clear off any debris from the sleeve’s injection and air-venting holes prior to use.

**Step 3:** Use a spacer (non-tacky flat, smooth disk with level surface) with known thickness to define the height of the cavity (Figure 14B) where the sample will reside. After the upper and lower rods are level with the spacer, tighten the upper and lower collets to fix both rods in place. The height and diameter of the cavity together determines the configuration factor (C-factor) of the sample ($C$-factor $= r/t$, where $r$ and $t$ are the radius and thickness of the cavity, respectively).
Step 4: Remove the spacer from between the rods, and adjust the alignment of the rods using the X-Y stage adjustment knobs on the lower collet fixture until the lower rod is vertically aligned with the upper rod. Slide the Teflon sleeve so that it is centered between the two rods (i.e. to the center of the cavity where the sample will reside) (Figure 14C).

Step 5: Position the curing light LED fixture underneath the lower quartz rod (such as shown in Figure 12A) to ensure the curing light flows directly through the rod to the sample. The LED should be centered and level underneath the lower rod, and should be positioned as close as possible to the rod.

Figure 14. Steps for the cavity preparation and testing setup configuration.

Step 6: Hold the photopolymerizable uncured material in a syringe tip so that it is ready to be inserted into the sleeve.

Now the NIST tensometer is ready to run a test and collect data, however, the instruments and the program that collects the data need to be setup as will be detailed in the next section.

2. Data collection

The collection of instrument data and control of irradiation are realized by a custom LabVIEW program developed at NIST. By running this program, changes in PS, DC, and exothermic temperature are monitored in real-time during photopolymerization and collected simultaneously and synchronously in LabVIEW at a user-defined sampling interval. The steps for running the NIST GUI are summarized by the following:

Open the graphical user interface: Start the Tensometer program by clicking on the shortcut icon in the startup menu or the icon in the 'Tensometer' folder of the user computer. The following window will appear:
Figure 15. Opening the LabVIEW interface of the tensometer.

This window will appear for approximately 2 seconds and then the following window will appear:

**Please Select Measurement, Curing Light, and Mode**

**STEP 1**
Please select if you want other measurements or calculations?

- Yes
- No

Measure temperature?

- Yes
- No

**STEP 2**
Please select curing light

- non-NIST curing light
- NIST curing light

For the non-NIST curing light, only the standard curing mode is available.

**STEP 3**
Please select curing mode

- Standard
- Ramp
- Two-step
- Pulse delay

Figure 16. Tensometer options for measurement, curing light and curing mode selection.

**Step 7a:** The two radio buttons shown in Figure 16 (Step 1) are used to control what will be measured during the test. During this step, users may include or exclude Degree of Conversion
and Temperature measurements. For this demonstration, we are going to include both these measurements. Note: PS is always measured by the program regardless of any button selections.

**Step 7b:** The two checkmark buttons shown in Figure 16 (Step 2) are used to control what type of curing light is used during the test. The user should click on the ‘non-NIST curing light’ button if the user is using a curing light source not provided by NIST. Please note if this option is chosen, then the power cord of the non-NIST curing light should be plugged into the one of the three controllable ports of the power USB. For this demonstration we are going to select the 'NIST curing light' option. The specific controls for irradiation in the ‘NIST curing light’ corresponding to the different curing modes are detailed in Step 8. For each combination of measurements, there are four curing modes (Standard, Ramp, Two-Step, and Pulse-Delay) available for selection by the user.

By clicking any one of the curing mode buttons (Standard, Ramp, Two-Step, and Pulse-Delay), a new window containing the corresponding LabVIEW main program for data acquisition for the specified mode will open (Figure 17). A window prompt may appear asking the user if he wants to import the last run values of the front panel. Click ‘Yes’ to import the last run values on to the front panel. For demonstration purpose, the simultaneous measurement of stress, conversion, temperature and ‘Standard’ curing mode are chosen to illustrate the operation of the tensometer program. For the other available tensometer curing mode configurations, the LabVIEW GUI display is almost identical except for some differences with the Irradiation Control options (see details in the following step).
Figure 17. Main window to input the parameters of the experimental setup for simultaneous measurement of stress, conversion, and temperature under ‘Standard’ curing mode.

Step 8: The tensometer LabVIEW graphical user interface shown in Figure 17 contains all the controls and inputs needed by the program to measure the stress, degree of conversion and temperature when the experiment starts. The different sections of this window will be discussed in the number they are ordered in the figure.

1. Curing mode: This button if clicked brings the Curing mode panel (Figure 16) back on screen. This is in case the user has incorrectly selected his option for measurements or curing mode the first time.

2. Check sensors: This control if clicked opens a window which allows the user to manually read the outputs from the sensors (temperature, laser and the displacement sensor). This is shown in Figure 18.
Figure 18. Checking the stress sensor, the laser light and the temperature sensor before starting the photopolymerization process.

The port/channel that each sensor is connected can be modified to ensure that communication to them is enabled through the software in this window.

3. Sample and Tensometer settings section: This section has multiple inputs for the dimensions of the sample and settings of the Tensometer.
   a. Diameter of sample (cm) [text-entry field]: Determined by the diameter of rods and the sleeve.
   b. Sample height (cm) [text-entry field]: Determined by the thickness of the spacer.
   c. Distance of sample along the beam, a (cm) [text-entry field]: Distance between sample position and fixed end (‘0 cm’ marking) of cantilever beam.
   d. Sampling interval (s) [text-entry field]: Time to collect one data point (for example, 0.2 of this interval means 5 data points per second). Suggested value $\geq 0.2$.
   e. Beam type [drop down selection]: There are currently three standard beam types that are present in the drop down (we have provided two beams for you, one compliant steel beam and a rigid steel beam). Please select the appropriate one that is currently set up on the Tensometer.
   f. Help [information button]: This control tells the user how to input the information of a new beam.
g. Material name [text-entry field]: Input name of the material being tested.

This section has two display boxes in the right column of this section which compute the C-Factor of the sample and the Compliance of the beam based on the inputs on the left hand side. These two boxes are only updated after the 'Start' button is clicked, so the user is requested to ignore the values shown in the boxes before the experiment starts.

4. Irradiation Control: Controls the irradiation conditions such as duration, intensity, etc. For the different curing modes available in Step 7, the parameters to control irradiation are different, as shown schematically in Figure 19. For all the curing modes, there is one parameter, the initial time (t0), controlling the start of irradiation relative to the start of data collection, i.e. no irradiation within time t0. The purposes of doing this to obtain a zero baseline (i.e. the average of the data collected within t0) for the development of PS, DC, and exotherm temperature. (Suggested value for t0 (s): 20; Suggested maximum light intensity depends on the maximum current rating of the LED)

5. Duration of experiment, Minutes [numeric-entry field] and Seconds (0-59) [text-entry field]: Duration for data collection.

6. Path to save data (Optional): Input the directory (including file name) where the data will be saved. For example, for the directory of ‘C:\temp\trial01.txt’, the data will be saved to the folder of ‘temp’ in the C disk drive and the file named as ‘trial01’. However, giving a path to save data is not compulsory. If this box is left empty, the default file name that is going to be created will be ‘Material name-HH-MM-SS’, where ‘Material name’ is from whatever is filed in the text box Material name, HH stands for the hours, MM stands for the minutes and SS stands for the seconds at which the experiment was run. The default file location for the file is in the ‘Analysis plots’ folder under the main program folder on the user desktop.

7. Additional comments on experiment [text-entry field] (Optional): Text can be entered here which the user may feel necessary to document regarding the experiment.

8. Absorbance [button]: Launches a new program window (‘NIR Initiation’) for collecting background spectrum, reference spectrum and the spectrum of the uncured sample. Additionally, the parameters for degree of conversion measurements are also set here. This new window will be discussed further in Step 5.

9. Import [button]: If you have previously collected all the necessary spectra then you can avoid clicking 'Absorbance' and click the 'Import' button and simply input all the necessary files as prompted by the program. The stored values are found in 'NIR Initiation data' folder under the main program folder on the user desktop. After this step, go directly to Step 11.
10. Save [button]: Click if you want to save every raw spectrum, captured at the speed of the sampling rate, as the material cures. (Raw spectrum is the full wavelength, 900-2200 nm, capture of the NIR spectrometer, eg. like the spectrum of the uncured sample shown in Figure 24)

11. Start [button]: Click to start the experiment and a new window titled ‘Analysis Plots of Experiment’ will open.

12. Stop [button]: Click if something went wrong to stop the Tensometer program.

**Figure 19.** Irradiation controls corresponding to different curing modes available.

**Step 9:** For experiments where the user specified the inclusion of degree of conversion measurements, next click the ‘Absorbance’ button in the NIR Control panel to start collecting background and reference spectra, as shown in Figure 20.
Step 10: After clicking on the ‘Absorbance’ button in Step 9, a new LabVIEW window will launch (Figure 21). The order in which these controls (buttons) are selected must follow a specific sequence (as described below) to collect the necessary information for the degree of conversion measurements. However, if the user misses a step, the program will remind the user to follow the necessary steps.

- Click ‘NIR spectrometer ready’ [button]: This is the first button that needs to be pressed. This controls the temperature of the spectrometer which is crucial to having a good signal to noise ratio. Ideally, when this button is pressed the mouse icon becomes a busy icon and the color bar above the button turns yellow, after a few seconds the color bar turns green and the mouse icon turns back to its default. This is when the user can proceed to the next bullet point in this step. Sometimes, when this button is pressed the mouse icon doesn’t change to the busy icon and there is no color change in the color bar. In such instances the user should press the button again, until the mouse turns into a busy icon.
- Scans to Average [text-entry field]: Numbers of scan to be averaged to get one spectrum. Default value: 2.
- Integration Time (ms) [text-entry field]: specify time to take a full range scan. Default value: 25.

Note: 1) The product of Scans to Average and Integration Time should be less than the sampling interval of the data collection.
2) The scans to average and integration time may be needed to be adjusted (generally increased) if using a more viscous material to reduce noise in the measurement.

- After making sure the optical fibers are aligned around the center of the sleeve as shown in Figure 23, click ‘Background Spectrum’ button to collect the dark background spectrum. When collecting the background spectrum, the IR beam from the IR light source (Figure 3A) should be turned off. A typical dark background spectrum collected is shown in Figure 21. Please note that the background spectrum can look different than the one shown in Figure 21.

![Figure 21. NIR initiation program after the background spectrum is collected (shown in orange).](image)

- Turn on the IR light source and click the ‘Reference Spectrum’ button to collect the reference spectrum for the Teflon sleeve. A typical reference spectrum collected is shown in Figure 22. Please note that the highest value on the y-axis should be generally be close to or above 40000 to indicate high signal to noise ratio.
If you have chosen temperature measurements as well, then this is an ideal time to setup the thermocouple wire by tightly twisting the two ends of the wire after removing the insulations. There is a 'Read Temp.' button in the bottom section of the window which can be used to read the temperature of the thermocouple. Ideally the thermocouple wire should read a normal room temperature of around 19-23°C.

- Slowly inject the sample into the cavity by squeezing the uncured paste (using a syringe tip) into the larger injection hole (not the air venting hole) in the Teflon sleeve until the void inside the sleeve is completely filled with the resin and no air bubbles exist inside the paste (Figure 23B). Clear off any excessive paste that may have overflowed during this injection process.
- If temperature measurement has been chosen to be measured, gently insert the microprobe thermocouple through the injection hole of the sleeve and into the center of the sample (Figure 23C). After inserting the thermocouple, click 'Read Temp.' again to check the thermocouple is reading a reasonable temperature close to 19-23°C. If the reading is not a reasonable number, then take out the thermocouple, tightly wound the two ends of the wire together and insert back into the sample and recheck the temperature. For highly viscous resins, a needle can be used to insert the thermocouple probe into the sample by threading the needle with the probe to guide the probe into the center of the sample. For a test where temperature will not be measured, skip this step.
Figure 23. Steps for setting up the optical cables for the IR light, inserting the sample and the thermocouple into the sleeve.

- Click the ‘Uncured Spectrum’ button in the NIR initiation window to start collecting sample spectra, as shown in Figure 24 for a typical dental composite sample. The user will be prompted to remind him/her to insert the thermocouple into the sample if the exotherm is being measured. Four graphs including the real-time spectra of the sample (‘Raw spectrum’), the specific peak selected for conversion calculation (‘Selected peak’, here the methacrylate C=C double bond is selected), the peak after baseline correction (‘Baseline correction’), and the calculated peak area based on data integration (‘Peak Area’), are displayed. In the ‘Selected peak’ graph, two cursors representing the start and end points of the peak can be adjusted by dragging them along the spectrum.

- After the peak area stabilizes (usually wait for the number of iterations indicator to reach 50), click the ‘Save’ button to save the background and reference spectra, the calculated peak area of uncured sample, and the defined start and end points of the peak (i.e. the position of the two cursors). This will also close the current NIR initiation program window and return control back to the ‘setup of experiment’ window (shown in Figure 17).
Figure 24. NIR initiation program during the collection of sample spectra.

Step 11: After returning to the setup of experiment window, click the Start button (as shown in Figure 17). If any of the sensors, for example the laser, is not responding in the intended manner the user will be alerted about it. The user can click on the 'Check sensors' button, labelled as 2 in Figure 17, to check and correct the error. If there are no errors, a new window titled 'Analysis Plots of Experiment' will open.

Step 12: The 'Analysis Plots of Experiment' window is waiting for the user to click the 'NIR spectrometer ready' button, similar to the one in the 'NIR Initiation' window. Once this button is pressed and the color bar turns green, the real-time development of PS, DC, and temperature, as well as the real-time NIR spectra will be displayed and recorded (Figure 2). The ‘Stop’ button is used to abort the data collection if the user needs to stop the program in the middle of the test. Otherwise, the program will run and automatically stop once the user-defined experimental time duration expires, and the data collected will be automatically saved.

3. Data report

After each experiment, the program will write one text file and two excel files into the directory defined during the test or in the default directory. These files include: filename.txt, filename-raw.txt, and filename-clean.txt, where filename represents the name of file defined.

- The first file, filename.txt in Figure 25, records all the experimental parameters for the test, such as combination of measurements, sample dimensions, irradiation mode and conditions, beam compliance, C-factor, and sample descriptions.
• The second file, filename-raw.csv, is a backup file which records the raw data collected during the test. It contains 6 columns (for combination measurement of stress, conversion, and temperature) as shown in Figure 26, with time, voltage of displacement sensor, shrinkage strain, shrinkage stress, conversion and temperature in sequence from left to right. In Figure 26, the first column, time, is the real-time starting from the beginning of data acquisition (i.e. time = 0 represents the color bar turned green in the 'Analysis Plots of Experiment' window).

• The last file, filename-clean.csv, is the final data of the test after certain treatments on the raw data, as shown in Figure 27. Such treatments include: 1) time shift, i.e. the first column, time, has been shifted forward by t0, which leads to time = 0 representing the time of irradiation start (instead of the time of data collection start in the raw data file); 2) zero baseline correction, where all the data shown in the final file has been adjusted by the zero baselines obtained by the averages of the data collected within time t0;

![Typical experimental parameters recorded by the tensometer program in a text file](image)

Figure 25. Typical experimental parameters recorded by the tensometer program in a text file
Figure 26. Typical raw data recorded by the tensometer program in an excel file.
4. After the test

After the measurements are completed (based on the test duration time specified by the user in the LabVIEW GUI), the tensometer program will be stopped automatically and all the data collected during the test will be automatically saved to the computer (directory location is specified in LabVIEW GUI, the default location of the file is in the 'Analysis plots' folder under the 'Tensometer' folder on the user computer) upon reaching the stop time of the experiment. The next step is to clean up the sample and get ready for the next test.

- Carefully cut the thermocouple probe wires to remove the thermocouple probe from the sample and cut away the Teflon sleeve from the sample using a razor blade.
- Remove the cured sample from between the rods by loosening the lower collet holder with one hand while using the other hand to grip the lower rod. Gently move the loosened rod downward
and away from the sample until the sample detaches from the rod. Remove the sample from the rod and set aside. Remove the remaining rod from the upper collet holder and set aside. If a loosened rod falls out of a collet holder, the rod could break; therefore, always grip a loosened rod with one hand to prevent this.

- Re-polish and re-silanize the rods for re-use if they were not damaged during the experiment and if the size of the rods after re-polishing are still 17.2 ± 0.2 cm.

5. Aborting during a test in-progress

There are several reasons for which a user may wish to stop an experiment that has already been started in LabVIEW. For example, if the material has not been properly inserted into the sleeve or if the degree of conversion plot (before the curing light is on) has a low Signal to Noise ratio. In such cases, the user should abort the test as soon as possible by clicking the ‘Stop’ button available in the current window that is being displayed.

After stopping the test and closing the window, the user may edit the LabVIEW test settings in the Setup of experiment window, if desired (see Step 4 of Data collection). Next, click on the ‘run’ (red arrow) button in the main LabVIEW program window. If the user already correctly captured the NIR initiation data prior to stopping the test, the user may click the ‘Import’ button to import the NIR (background, reference and spectrum) collection since it was already saved; else the user should click ‘Absorbance’ (see Step 10 of Data collection) and repeat the initiation. Next, the user may re-start the test by clicking the ‘Start’ button. If prompted, click ‘Ok’ to overwrite any existing file.

References


NIST Technical Support: (301) 975-5186 or martin.chiang@nist.gov
Appendix

A1. Part Vendor Information
Information for the manufacturers of quartz rods and Teflon sleeve

- Quartz rods

(1) National Scientific Company
P.O. Box 498 Quakertown, PA 18951 USA
Phone: (215) 536-2577 Fax: (215) 536-5811
www.quartz.com

(2) Quality Quartz of America, Inc.
9362 Hamilton Drive, Mentor, OH 44060
Phone: (440) 352-2851 Fax: (440) 352-2871
www.qualityquartz.com

- Teflon sleeve

(1) Tef Cap Industries Inc.
Park Valley Corporate Center
1155 Phoenixville Pike Suite 103 West Chester, PA 19380
Phone: (610) 692-2576 Fax: (610) 430-0116
www.tefcap.com

(2) Zeus Industrial Products, Inc. (Engineered Extrusions Division)
Phone: (803) 268-5223 Fax: (803) 533-5694
Cameron Rast, Email: erast@zeusinc.com
PTFE; Extruded Tube; AWG3; Standard Wall 6/7 mm (ID/OD)
Zeus Part # 14531
www.zeusinc.com

(3) Fluorostore
www.fluorostore.com
PTFE Tubing - Metric (mm) / 4 mm ID X 5 mm OD
PTFE Tubing - Metric (mm) / 5 mm ID X 6 mm OD

- Thermocouple probe

(1) Physitemp Instruments, Inc.
http://www.physitemp.com
154 Huron Avenue, New Jersey 07013
Phone: (973) 779-5577 / Toll Free: (800) 452-8510 / Fax: (973) 779-5954
• Stainless steel weights for calibration

http://www.troemner.com/
201 Wolf Drive, Thorofare, NJ 08086
Phone: (800) 352-7705

A2. Troubleshooting Tips

The following are some details to check to ensure that the experimental set-up is correct.

√ Is the Thermoelectric Cooler (TEC) button powered ON (i.e. indicator illuminated in blue) for the Arroyo Combosource Controller?
√ Are the thermocouple wires properly coupled together (i.e. twisted pair is making good contact)? This can be checked by clicking the ‘Check sensors’ button on the ‘Setup of experiment. vi (Figure 18)’
√ If measuring temperature during the experiment, is the probe inserted into and centered within the sample via the injection hole in the sleeve? This needs some practice especially if the sample is very viscous
√ Is the voltage reading on the displacement probe nearly zero when the probe is not being displaced (i.e. when the probe is at its baseline position)? This can be checked in the ‘Check sensors’ window (Figure 18)’