

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

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Introduction	2
Instrument components and software installation	4
Testing mechanics	6
Calibration	9
Testing procedures	11
1. <i>Sample preparation</i>	11
2. <i>Data collection</i>	14
3. <i>Data report</i>	23
4. <i>After the test</i>	25
5. <i>Aborting during a test in-progress</i>	26
References	26
Appendix	27

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

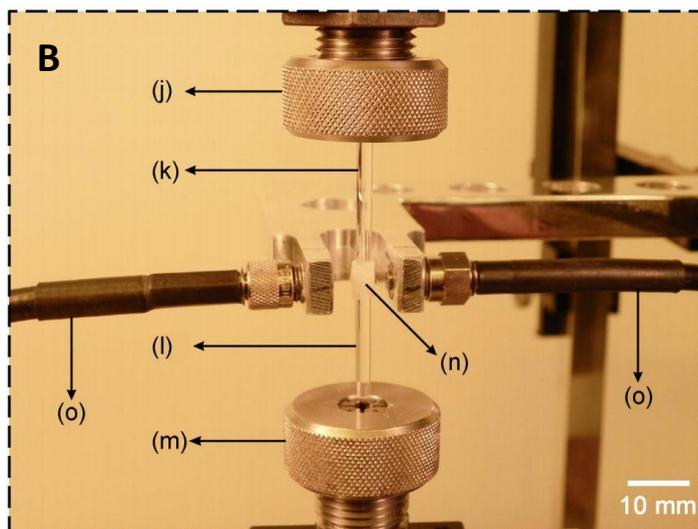
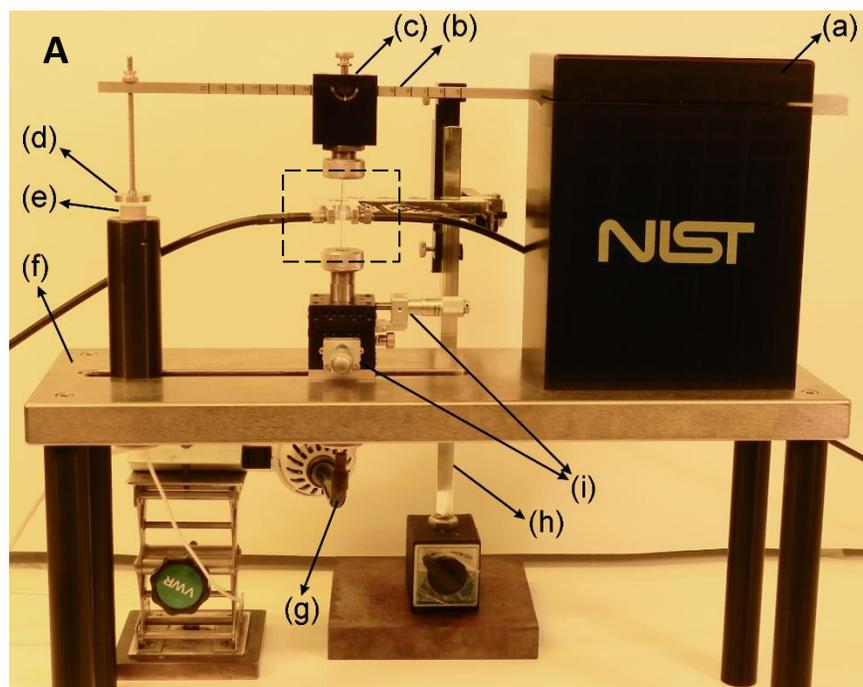
Introduction

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) used for measurement and data acquisition during a photopolymerization experiment using the instrument.



- (a) cantilever-beam holder
- (b) cantilever beam
- (c) upper collet holder
- (d) flat metal target
- (e) probe of displacement sensor
- (f) base stand
- (g) curing light guide
- (h) NIR cable holder
- (i) X-Y stages
- (j) upper collet
- (k) upper quartz rod
- (l) lower quartz rod
- (m) lower collet
- (n) sample encased by PTFE sleeve
- (o) NIR optical fibers

Figure 1. Photographs 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.

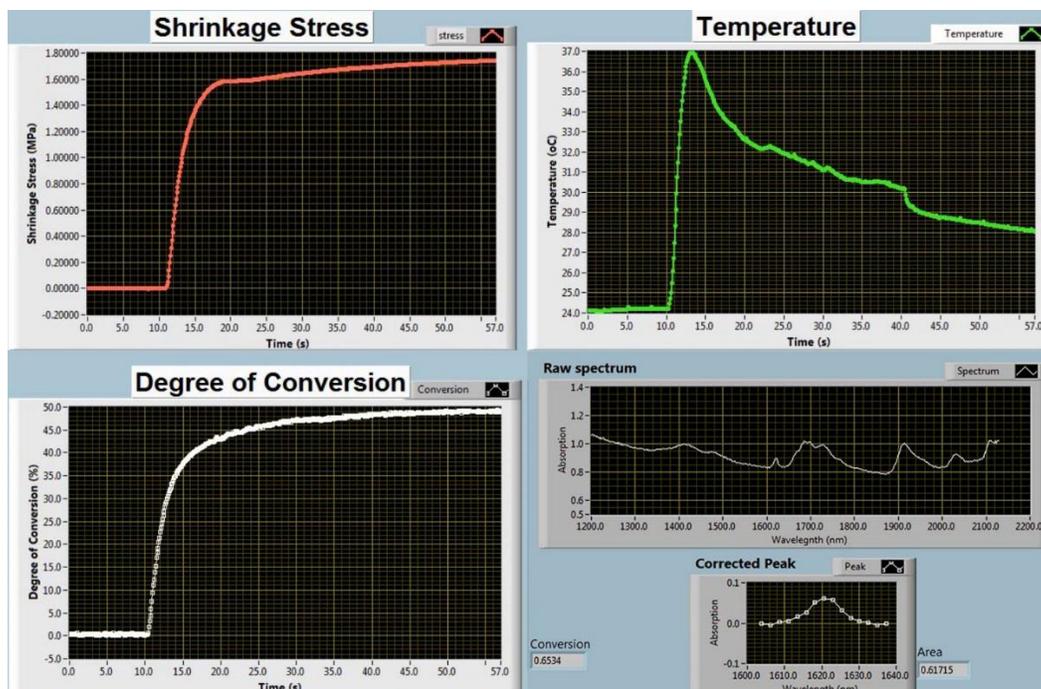


Figure 2. NIST tensometer GUI for data acquisition shown with curing light switched on at 10 seconds and off at 40 seconds for demonstration purposes.

Instrument components and software installation

The NIST tensometer (see 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:

- Near infrared (NIR) spectrometer (NIRQuest512-2.2, Ocean Optics) and infrared (IR) light source (HL-2000, Ocean Optics) for spectra monitoring (Figure 3A).
- 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 including a controller (6340 ComboSource, Arroyo Instruments) and LED light (LZ1-10DB00, LED Engin) (Figure 3D). The curing light selected here is a single blue color LED, which emits a spectrum with concentrated peak centered near 465 nm, as shown in Figure 4. This spectrum matches well with the absorption of 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).

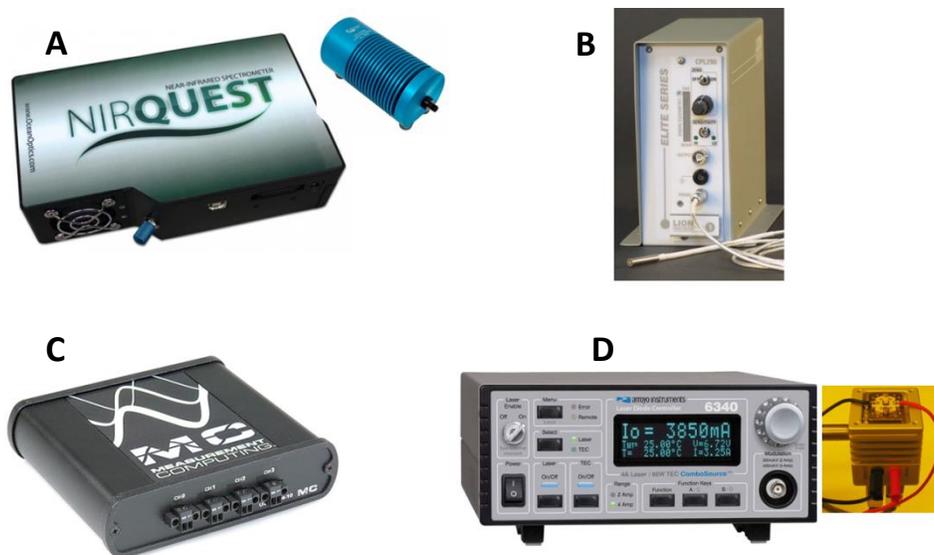


Figure 3. Devices integrated with NIST tensometer system. (A) NIR spectrometer [left] and IR light source [right]; (B) Driver of displacement sensor; (C) DAQ device; and (D) Curing light system [right] and its controller [left].

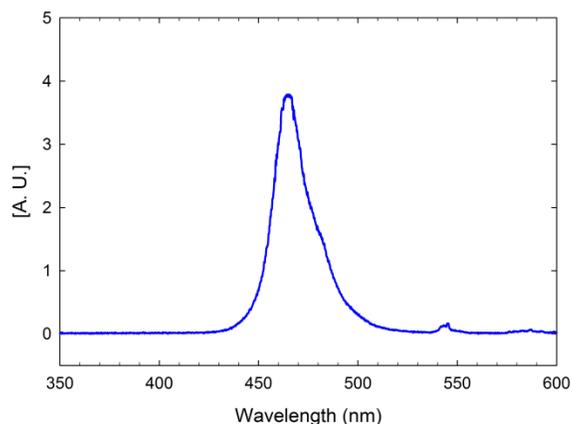


Figure 4. Spectrum of the curing light selected for CQ/amine-based materials.

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 software (including LabVIEW Windows 32-bit Full Development System and LabVIEW Windows 32-bit MathScript RT Module, version 2013 or later) and device drivers have to be properly 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.

Testing mechanics

A simple schematic for the tensometer is shown in Figure 5A. 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, with 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 for the manufacturer information) 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 5B), 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:

$$\sigma = \frac{F}{A} = \frac{6\delta EI}{\pi r^2 a^2 (3l - a)} \quad (1)$$

where σ 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; δ is the beam deflection at the free end; $E = 203$ GPa and $I (= wh^3/12, w = 6.38$ mm, $h = 12.68$ mm) 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, respectively; $l (= 24.5$ cm) and a are the length of the beam measured from the '0 cm' marking to the metal target (shown in Figure 1B) and the distance between the sample position and the clamped edge of the beam, respectively.

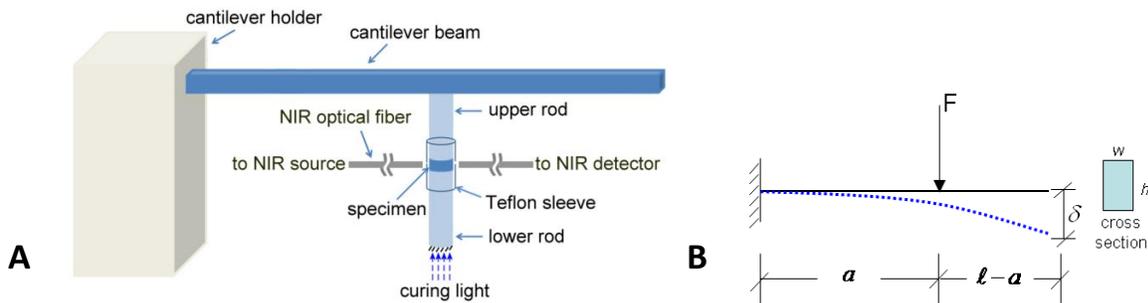


Figure 5. (A) Schematic diagram of the instrument for simultaneous measurement of polymerization stress and curing kinetics (with temperature measurement not shown). (B) Schematic of the cantilever beam configuration for polymerization stress measurement.

The NIR data acquisition is realized by configuring two optical-fiber cables (preferably 1 mm in diameter or close) 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 in 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=C-H stretching, first overtone) is used (see Figure 6). 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 ($Area_{monomer}$) and at each time point during the photopolymerization process ($Area_{polymer}$) based on the following formula:

$$DC = \left(1 - \frac{Area_{polymer}}{Area_{monomer}} \right) \times 100\% \quad (2)$$

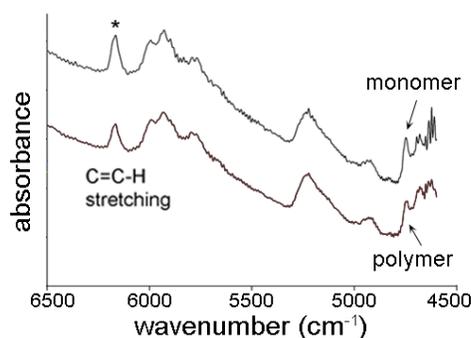


Figure 6. Typical spectra of methacrylate materials before and after photopolymerization. Absorptions associated with the methacrylate $=\text{CH}_2$ bonds (first overtone) are highlighted by the asterisk at 6165 cm^{-1} .

Temperature of the sample during the photopolymerization process is measured using a microprobe thermocouple (0.1 mm diameter, Physitemp Instruments) inserted into the center of the specimen (Figure 7) 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 rewired for reuse after each experiment by carefully stripping the wire insulation and twisting the ends together.

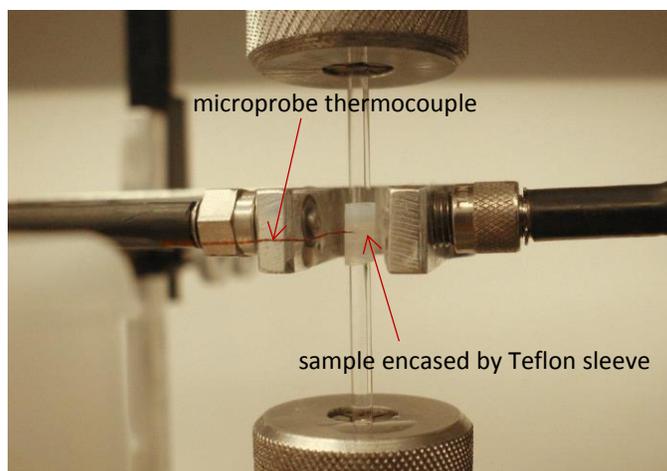


Figure 7. Photograph showing the measurement of temperature using a microprobe thermocouple.

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 latter factor can be determined by applying a second irradiation (to the post-cured sample) of the same irradiation conditions as those imposed during curing of the sample. Figure 8 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 two-step irradiation method.

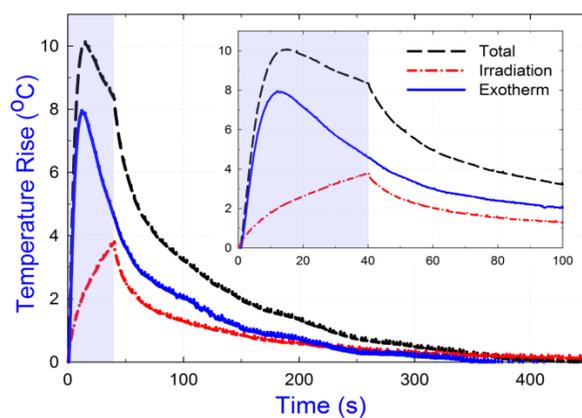


Figure 8. Reaction exotherm measured by a two-step irradiation method. Shaded areas indicate irradiation time.

Calibration

- Displacement sensor

The displacement sensor used in the tensometer system is a capacitive sensor with 20 nm resolution (data provided by the manufacturer). 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 (see Figure 1) 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 deadweight (fishing sinker) with constant known weight (P), as shown in Figure 9A. For each hanging location along the beam from the clamped beam edge (a), a sensor voltage reading (ΔV) 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:

$$\delta = \frac{Pa^2(3l - a)}{6EI} \quad (3)$$

where the parameters are the same as those defined in Equation (1). The voltage reading is then plotted against the calculated deflection as shown in Figure 9B. Linear fitting ($y = mx+b$) of the data points gives a slope of 10.3627 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.

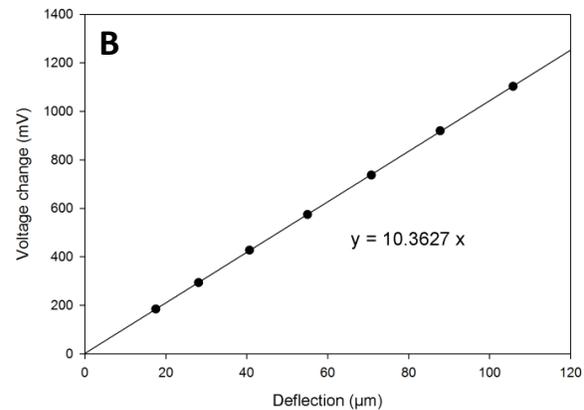
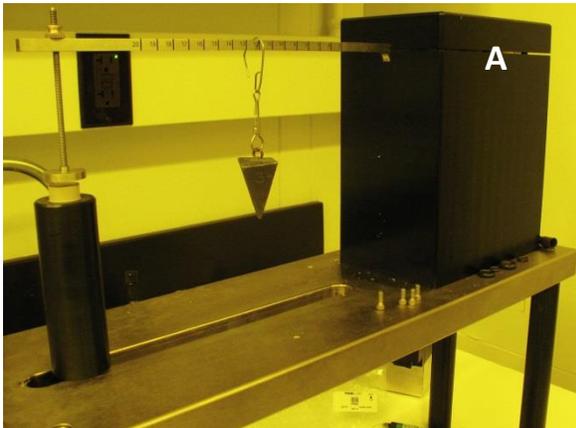


Figure 9. (A) Photo of NIST tensometer with deadweight for displacement sensor calibration. (B) Calibration plot of the voltage reading from the displacement sensor vs. the calculated beam deflection. The solid line is a linear fit of the data.

- 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/cm^2 , 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/cm^2).

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 10A. 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 10B. The correlation between current and intensity is non-linear and a simple hyperbola equation ($y = ax/(b+x)$) is used to fit the data. The two fitting coefficients (a and b) are used to convert current to light intensity in the tensometer's LabVIEW program. For the blue LED light (spectrum shown in Figure 4), calibration coefficients for a 2.5 mm-diameter sample were $a = 7007.67$ and $b = 1750.08$. For a 6 mm-diameter sample, the calibration coefficients were $a = 6314.22$ and $b = 2416.38$. The light intensity calibration is recommended whenever a new curing light bulb is installed in the tensometer system or the sample diameter size (quartz rod diameter) is changed. 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.

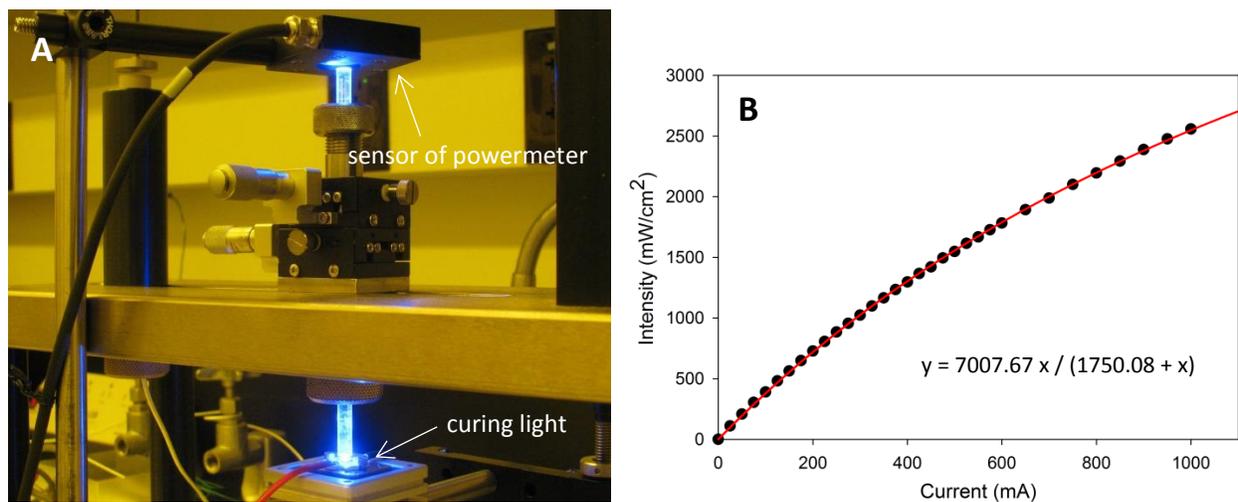


Figure 10. (A) Photo showing the calibration set-up for curing light intensity. (B) Calibration plot of the light intensity (using 2.5 mm rod) vs. input current. The solid line is a hyperbolic fit of the data.

Testing procedures

1. Sample preparation

Before the uncured sample to test is injected into a prepared ‘cavity’ (*i.e.* gap between two quartz rods encased by the Teflon sleeve) through a syringe setup, there are several preparation steps required for the experiment. Since uncured samples are photo-reactive, 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. Additionally, quartz rod ends should be polished and silanized prior to running experiments. 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 usage.

The steps for the preparation of the ‘cavity’ and configuration of the testing setup are summarized as follows:

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 (see Figure 11) 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:

$$C = \frac{a^3}{3EI} \quad (4)$$

where C ranges from 0.33 $\mu\text{m}/\text{N}$ to 12.12 $\mu\text{m}/\text{N}$ 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.

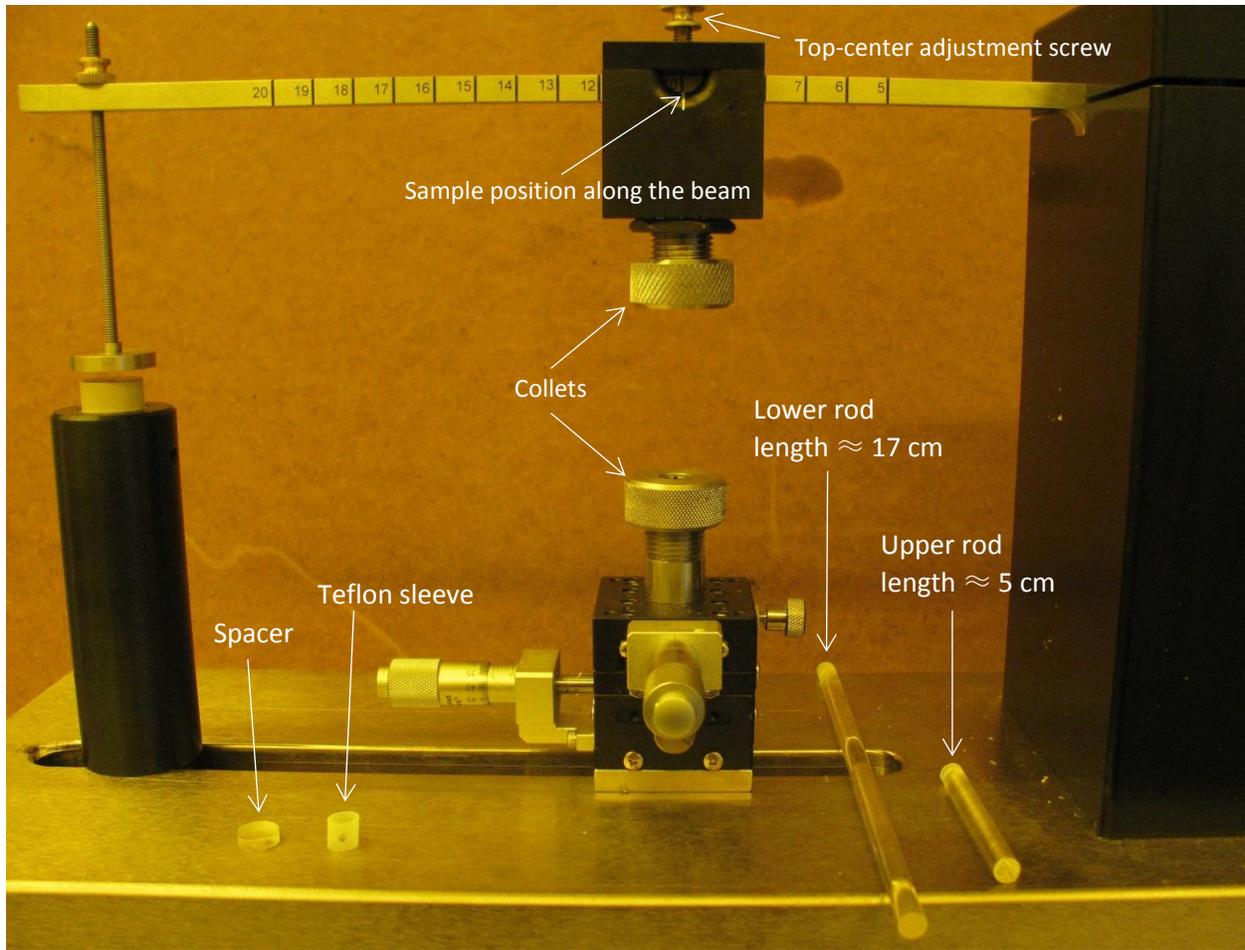


Figure 11. Preparation for a test using the tensometer.

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. To obtain better test results, the rod ends should be polished flat and smooth before silanization. The upper and lower rod lengths are shown in Figure 11. Slide a Teflon sleeve (with same diameter as rod) onto either one of the two rods (Figure 12A). 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 and any debris should be cleaned 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 12B) 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 ($C\text{-factor} = r/t$, 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 12C).

Step 5: To prepare for degree of conversion (DC) measurements with the tensometer, configure the optical-fiber cables onto the sides of the cavity by positioning the cables in the cable mount such that the IR light beam and detector reading will pass through the center of the cavity (Figure 12D). Perform Step 1 through Step 6 in the following section of this document (Testing procedures, Section 2. Data Collection) to collect the background and reference spectra for the Teflon sleeve using the tensometer LabVIEW GUI. For experiments where DC will not be measured, skip this step.

Step 6: 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 12E). Avoid overfilling the sleeve with excess paste as this may cause the paste to overflow out of the injection and vent holes.

Step 7: Gently insert the microprobe thermocouple through the injection hole of the sleeve and into the center of the sample (Figure 12F). The thermocouple wires should be tightly coupled together and the probe operation should be tested prior to insertion into the sample. To verify the thermocouple operation prior to an experiment, a digital multimeter (capable of reading miniature thermocouple connectors [type SMP]) can be used to read the measured room temperature of the thermocouple probe. 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.

Step 8: Position the curing light LED fixture underneath the lower quartz rod (Figure 10A) 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.

Now the NIST tensometer is ready to run a test and collect data.

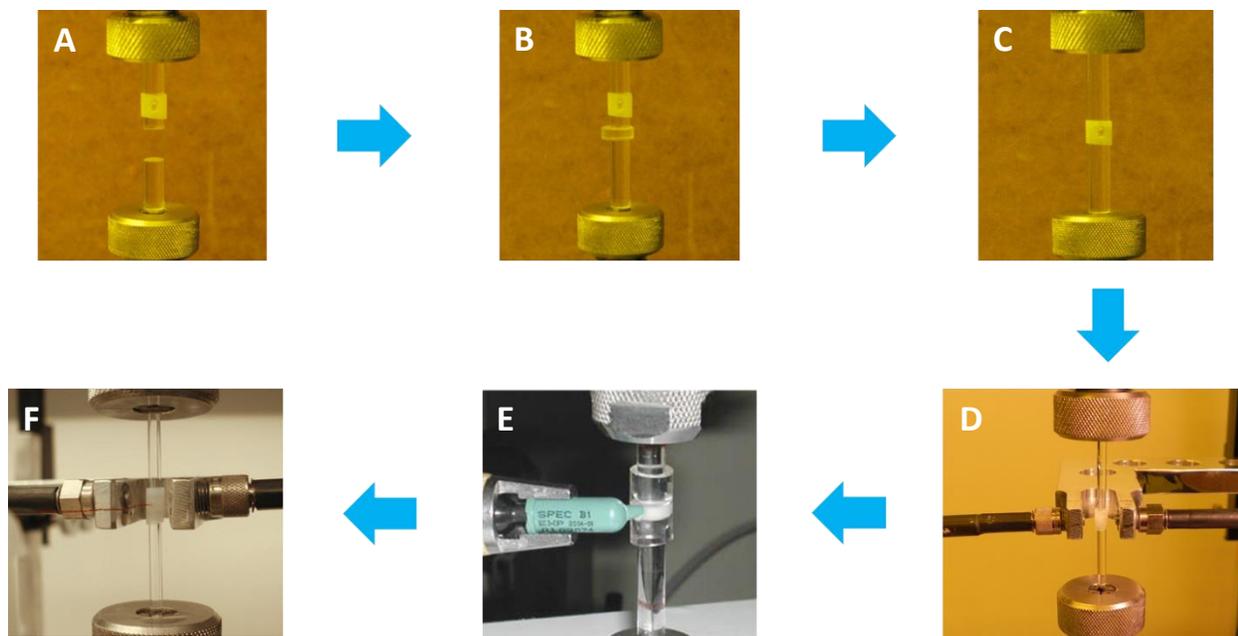


Figure 12. Steps for the cavity preparation and testing setup configuration.

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 speed. The steps for running the NIST GUI program are summarized as following:

Step 1: Start the ‘Tensometer_opener’ program by clicking on the shortcut icon on the desktop of the user computer (requires LabVIEW Full Development System and MathScript RT Module, 32-bit Windows version 2013 or later installation). The following window will appear:

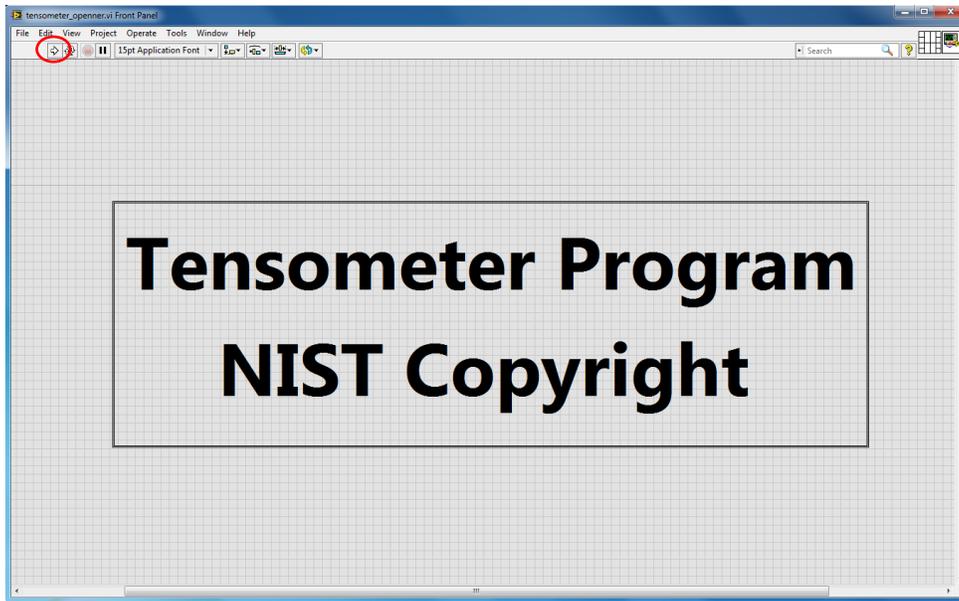


Figure 13. Opening the LabVIEW interface of the NIST GUI program.

Step 2: Run the tensometer program by clicking the ‘run’ button (arrow button) as circled in red in Figure 13. This will open up a new window prompt requesting the user to choose the measurement and curing mode, as shown in Figure 14. The two vertical slide switches are used to control the parameters that will be measured during the test. Based on the user-defined positions of the two slide switches (*i.e.* Yes or No), there are four options for specifying the parameters to be measured during the tensometer experiment: (1) stress + conversion + temperature (default - both switches set to Yes), (2) stress + conversion (‘with temperature’ set to No), (3) stress + temperature (‘with conversion’ set to No), or (4) stress only (both switches set to No). For each combination of measurements, there are four curing modes (Standard, Ramp, Two-Step, and Pulse-Delay) available for selection by the user. The specific controls for irradiation corresponding to the different curing modes are detailed in the following Step 4.

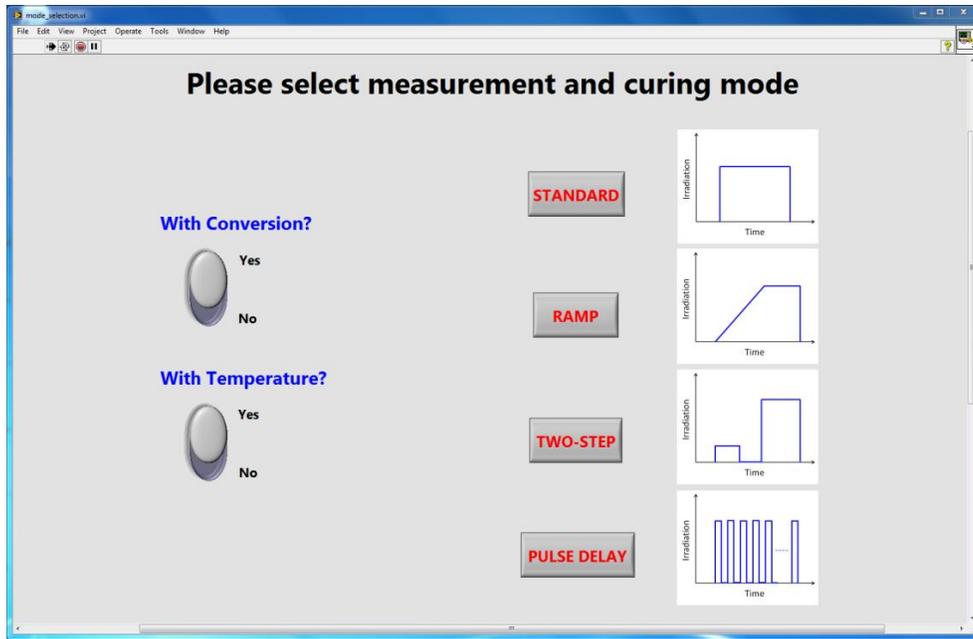


Figure 14. Tensometer LabVIEW GUI for measurement and curing mode selection.

Step 3: 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 15). Only one curing mode should be launched at any one time. For demonstration, the default slide switch measurement settings (*i.e.* simultaneous measurement of stress, conversion, and 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).

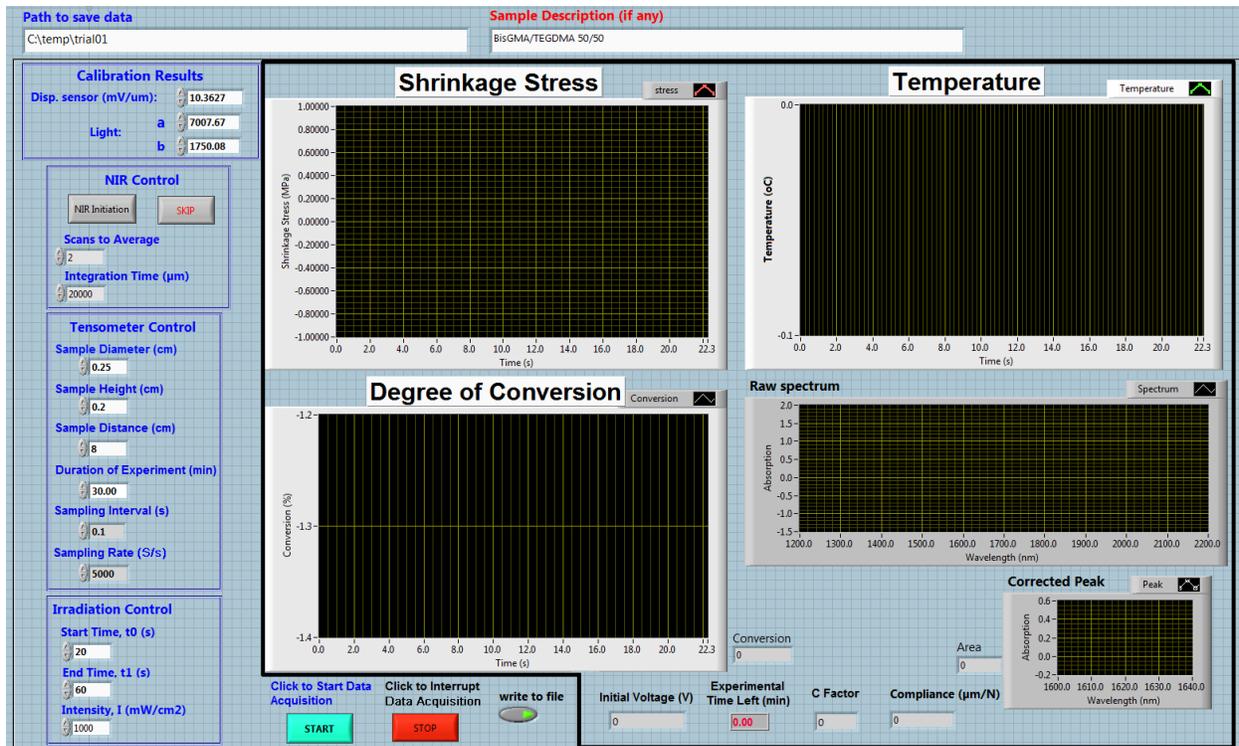


Figure 15. Main data acquisition program for simultaneous measurement of stress, conversion, and temperature under STANDARD curing mode with default parameters enabled. Items inside the **black** frame are indicators (displays) while those outside (*e.g.* buttons, text-entry fields) are controls.

Step 4: The tensometer LabVIEW graphical user interface shown in Figure 15 contains controls (outside the black frame) and indicators (inside the frame). Before running an experiment, all the following controls in the LabVIEW GUI have to be specified by the user:

- Path to save data [text-entry field]: input the directory (including file name) where the data will be saved. For example, for the directory of ‘C:\temp\trial01’, the data will be saved to the folder of ‘temp’ in the C disk drive and the file named as ‘trial01’.
- Sample description (optional) [text-entry field]: input any descriptions about the sample, test, or any other information to distinguish the test.
- Calibration results [text-entry fields]: input the self-calibration value (slope m) of the displacement sensor (see Figure 9B) and the two coefficient values (a and b) obtained from the calibration of light intensity (see Figure 10B). Default values: Disp. sensor (mV/ μm): 10.3627; a : 7007.67; and b : 1750.08 (corresponding to the rod size of 2.5 mm).
- NIR Control: controls of the NIR spectrometer.
 - NIR Initiation [button]: launch a new program window for collecting background and reference spectra as well as setting parameters for conversion measurements.
 - Skip [button]: skip the NIR Initiation program (if desired, apply this to a test to skip collection of background and reference spectra)

- Scans to Average [text-entry field]: numbers of scan to be averaged to get one spectrum. Default value: 2.
- Integration Time (μs) [text-entry field]: specify time to take a full range scan. Default value: 20000.

Note: the product of Scans to Average and Integration Time should be less than the sampling interval of the data collection (see below).

- Tensometer Control: controls the sample dimensions and data acquisition rates.
 - Sample diameter (cm) [text-entry field]: determined by the diameter of rods and sleeve
 - Sample height (cm) [text-entry field]: determined by the thickness of spacer
 - Sample distance (cm) [text-entry field]: distance between sample position and fixed end ('0 cm' marking) of cantilever beam
 - Duration of experiment (min) [text-entry field]: duration for data collection
 - Sampling interval (s) [text-entry field]: time to collect one data point (for example, 0.1 of this interval means 10 data points per second). Suggested value: ≥ 0.1
 - Sampling rate (Samples/s) [text-entry field]: sampling rate of the DAQ device (maximum: 50,000; default: 5000)
- Irradiation Control: controls the irradiation conditions such as duration, intensity, *etc.* For the different curing modes available in Step 3, the parameters to control irradiation are different, as shown schematically in Figure 16. For all the curing modes, there is one parameter, the initial time (t_0), controlling the start of irradiation relative to the start of data collection, *i.e.* no irradiation within time t_0 . The purposes of doing this are: 1) to leave some time to check the test inputs before the photopolymerization reaction starts; and 2) to obtain a zero baseline (*i.e.* the average of the data collected within t_0) for the development of PS, DC, and exotherm temperature. (Suggested value for t_0 (s): 20; Suggested maximum light intensity (mW/cm^2): 4000)
- Data Logging Control: turns on or off the write to file (data logging) capability for the main program.
 - Write to file [button]: toggle button used to turn data logging on or off during a test. Button is green when logging is enabled and grey when logging is disabled. Default setting: enabled (green).

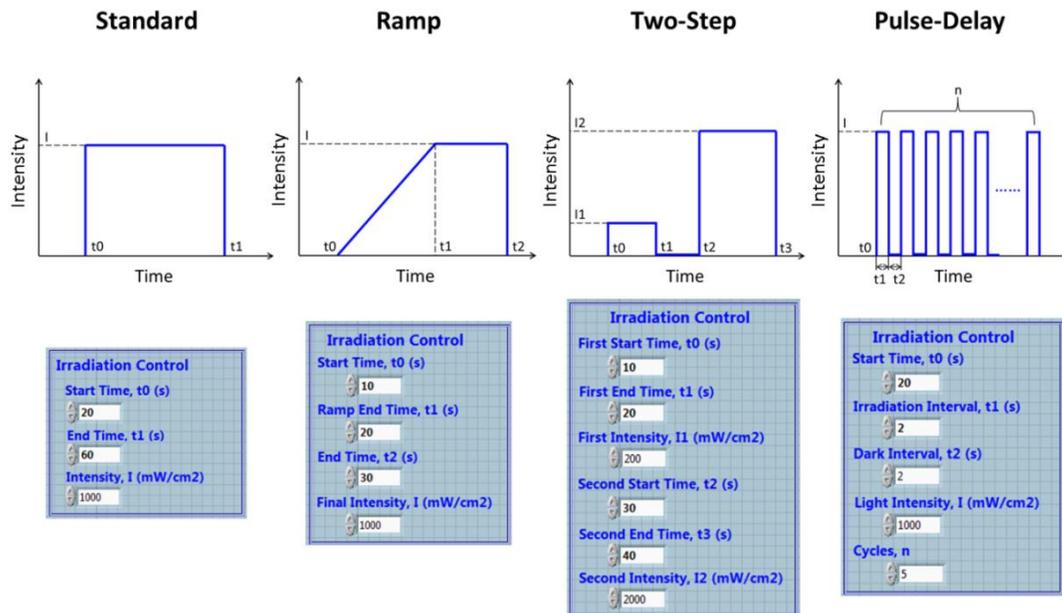


Figure 16. Irradiation controls corresponding to different curing modes available.

Step 5: After all the controls are specified by the user, click the ‘run’ (red arrow) button in the main LabVIEW program window to set the controls settings in place. For experiments where the user specified the inclusion of degree of conversion measurements, next click the ‘NIR Initiation’ button in the NIR Control panel to start collecting background and reference spectra, as shown in Figure 17. For a test without collecting the background and reference spectra, click ‘Skip’ (instead of ‘NIR Initiation’) in the NIR Control panel and go directly to Step 7. (**Important:** for tests with degree of conversion measurements included, all the steps stated above should be performed before the injection of sample into the Teflon sleeve, *i.e.* right after completing Step 5 [Figure 12D] in the Testing procedures, Section 1. Sample Preparation section of this document.)

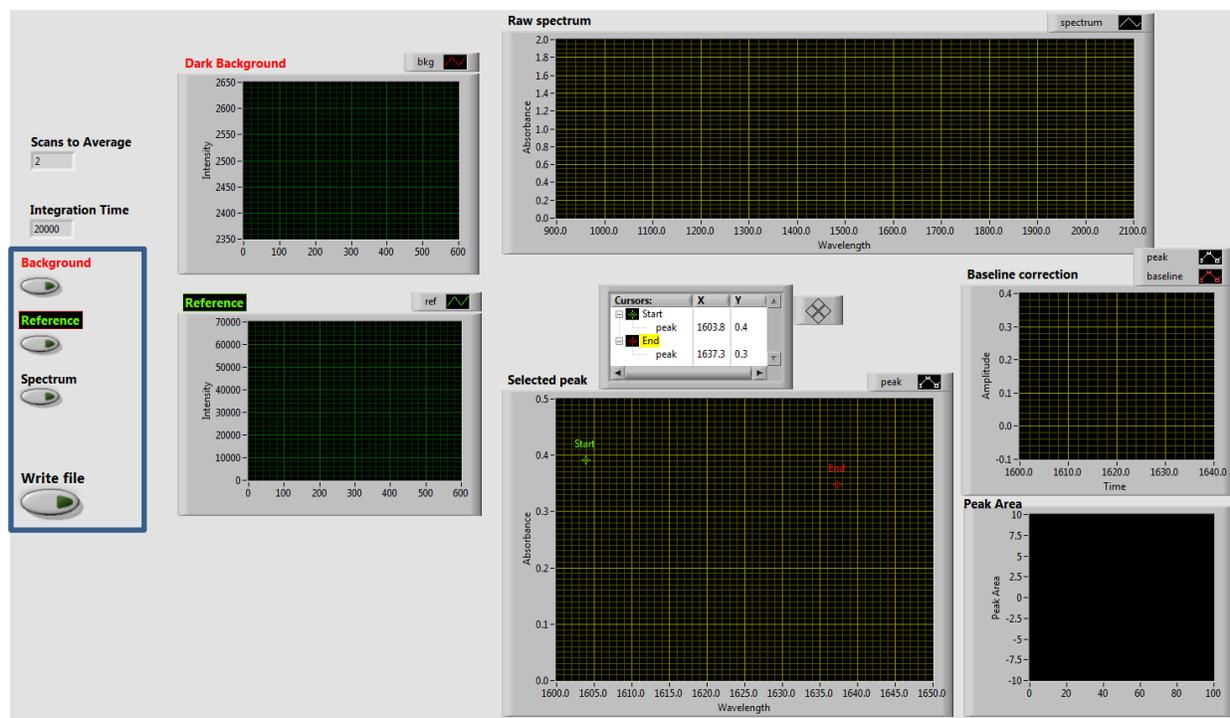


Figure 17. NIR initiation program for collecting background spectrum, reference spectrum, and peak area of uncured sample. Items inside the **black** frames are controls and the rest are indicators (displays).

Step 6: After clicking on the ‘NIR Initiation’ button in Step 5, a new LabVIEW window will launch. There are 4 control buttons in the newly-launched window (see Figure 17): ‘Background’, ‘Reference’, ‘Spectrum’, and ‘Write file’. 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.

- Click ‘Background’ 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 18.

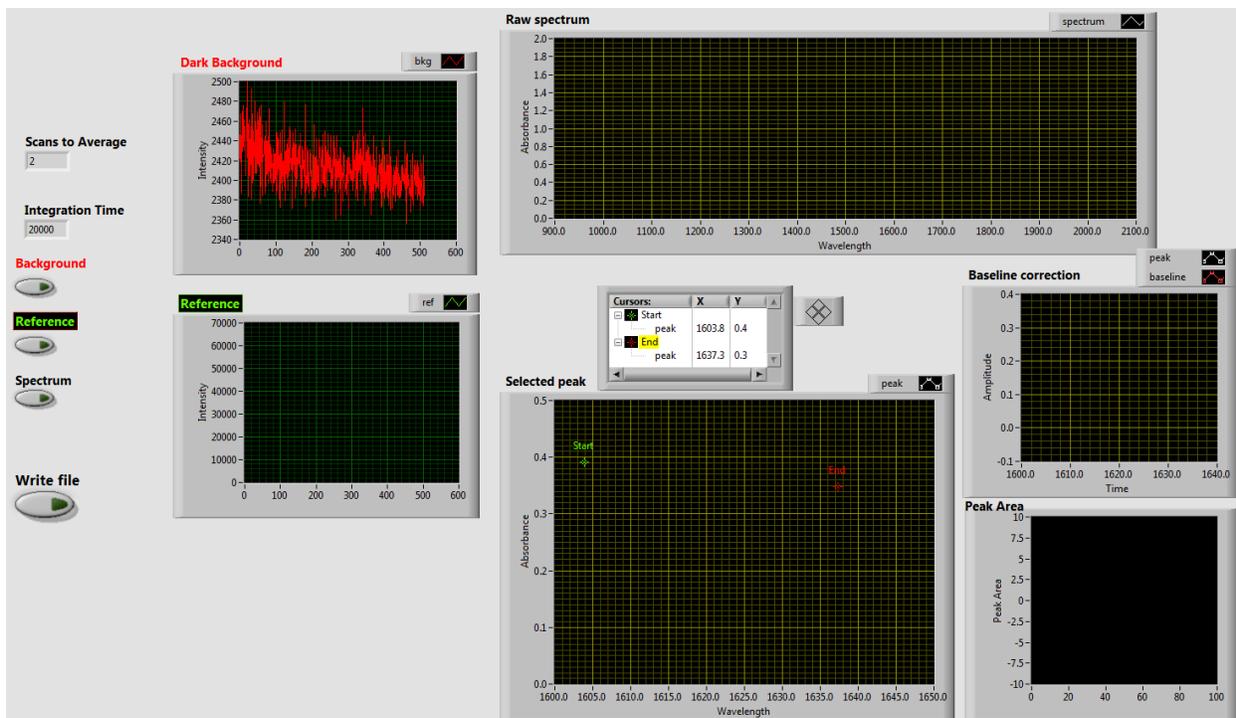


Figure 18. NIR initiation program after the background spectrum is collected (shown in red).

- Turn on the IR light source and click the ‘Reference’ button to collect the reference spectrum for the Teflon sleeve. A typical reference spectrum collected is shown in Figure 19.

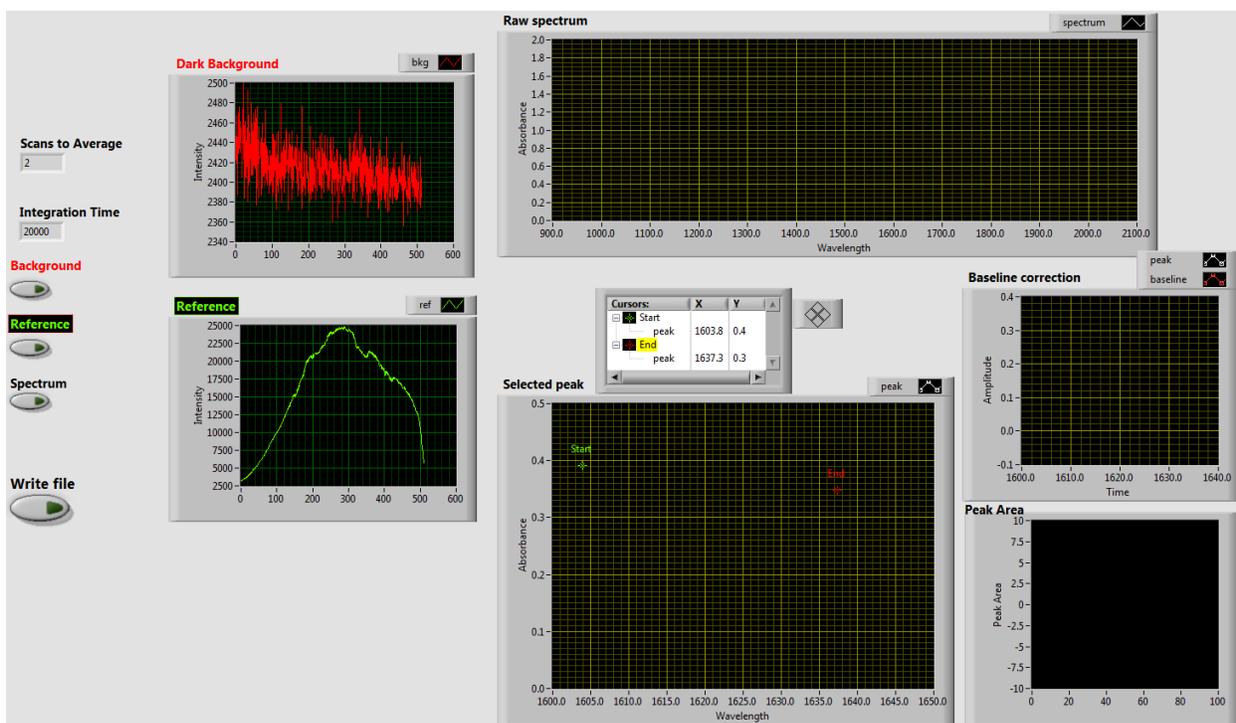


Figure 19. NIR initiation program after the reference spectrum is collected (shown in green).

- At this time, leave the NIR initiation window open, return to the Testing procedures (Section 1. Sample Preparation) in this document, and complete the remaining steps in the Sample Preparation section (*i.e.* Step 6 through Step 8). After the Sample Preparation steps in Section 1 are completed, click the ‘Spectrum’ button in the NIR initiation window to start collecting sample spectra, as shown in Figure 20 for a typical methacrylate sample. 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 a few seconds after clicking the ‘Spectrum’ button), click the ‘Write file’ button to output 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) to the file specified in Step 4. This will also close the current NIR initiation program window and return control back to the main program as shown in Figure 15.

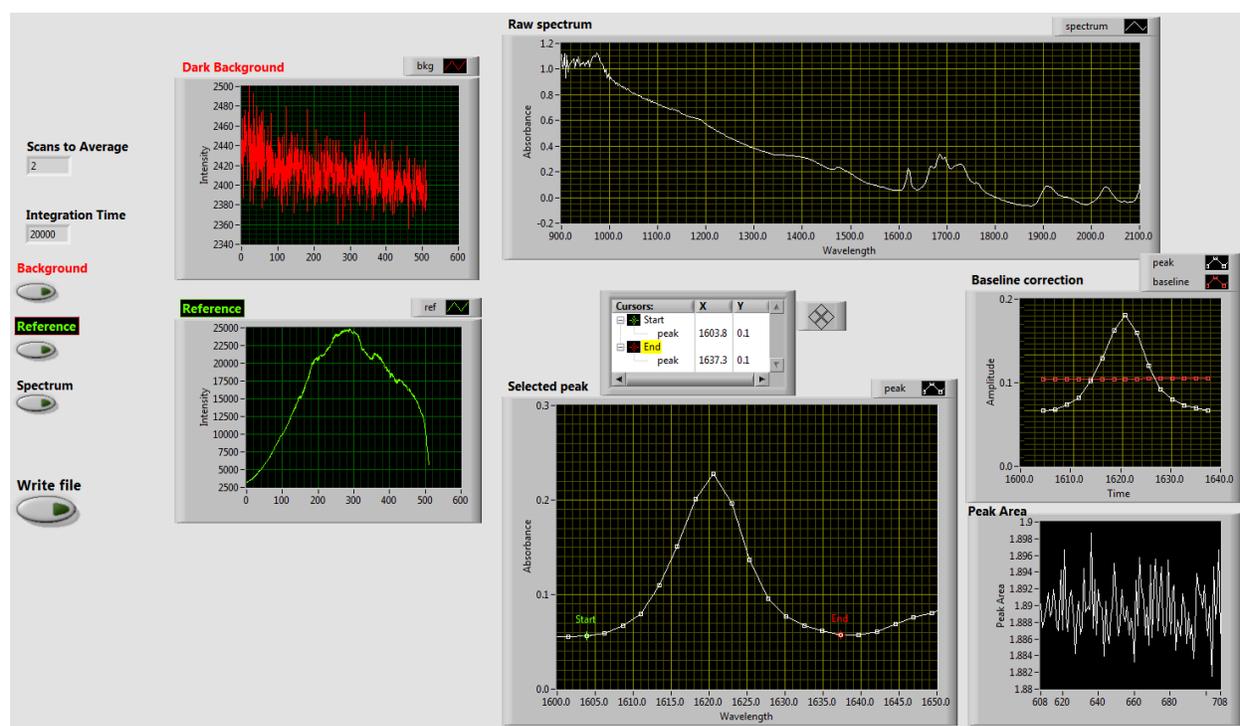


Figure 20. NIR initiation program during the collection of sample spectra.

Step 7: After returning to the main program, wait a few seconds until the displacement sensor is initialized (*i.e.* a number appears in the ‘Initial Voltage (V)’ indicator). Click ‘Start’ button (see Figure 15) to start collecting data. The real-time development of PS, DC, and temperature, as

well as the real-time spectra will be displayed (see Figure 2). The ‘Stop’ button in the main program (Figure 15) 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 to the directory defined in Step 4.

3. Data report

After each experiment, the program will write three plain text files into the directory defined during the test. These files include: filename-experiment conditions.txt, filename-raw.txt, and filename.txt, where filename represents the name of file defined.

- The first file, filename-experiment conditions.txt in Figure 21 (with example filename ‘rigid run1’), 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.txt, is a backup file which records the raw data collected during the test. It contains 5 columns (for combination measurement of stress, conversion, and temperature) as shown in Figure 22, with time, shrinkage stress, voltage, temperature, and conversion in sequence from left to right. In Figure 22, the first column, time, is the real-time starting from the beginning of data acquisition (*i.e.* time = 0 represents the time when the ‘Start’ button is clicked in Figure 15).
- The last file, filename.txt, is the final data of the test after certain treatments on the raw data, as shown in Figure 23. Such treatments include: 1) time shift, *i.e.* the first column, time, has been shifted forward by t_0 , 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 t_0 ; and 3) addition of sample deformation column (the fifth column) into the file to show the sample height change during polymerization.

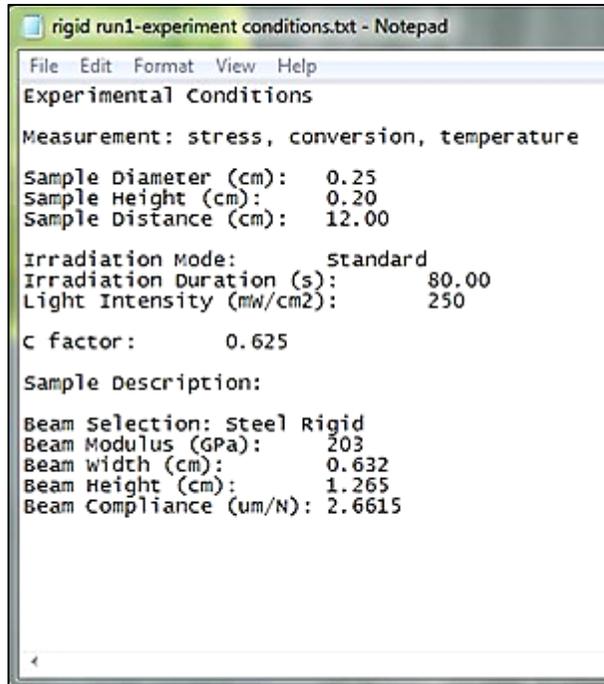


Figure 21. Typical experimental parameters recorded by the tensometer program.

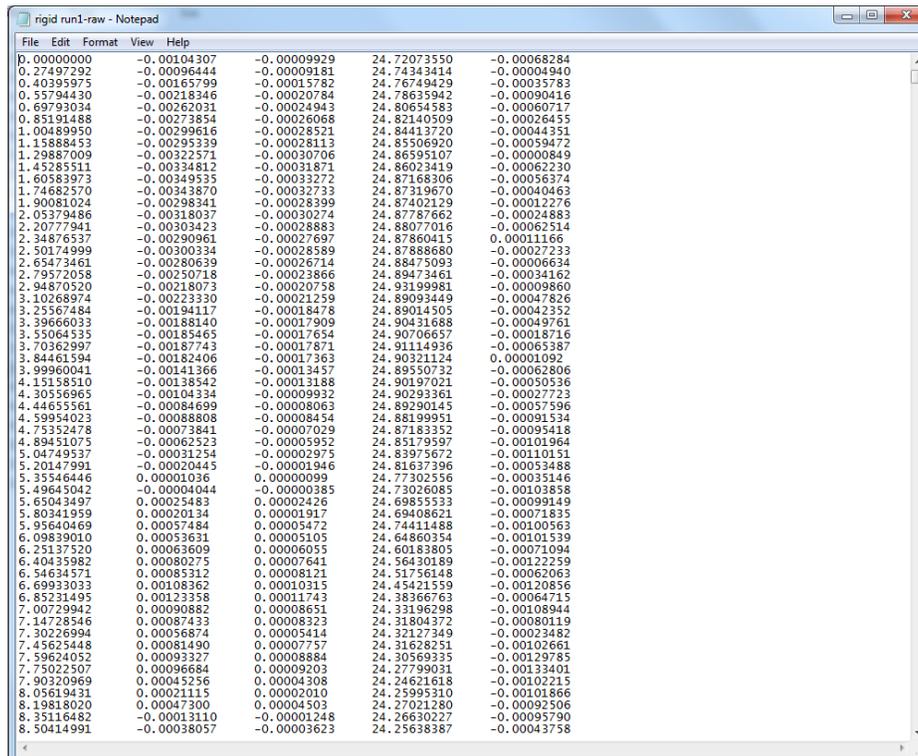


Figure 22. Typical raw data recorded by the tensometer program.

time (s)	stress (MPa)	voltage (V)	temperature change(°C)	sample deformation (mm)	Degree of Conversion
0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
0.0479909	0.0016584	0.0013787	-0.0604836	0.0000121	0.0036659
0.2009791	0.0018381	0.0017497	-0.0664584	0.0000220	0.0036319
0.3539648	0.0019904	0.0018947	-0.0659549	0.0000245	0.0011087
0.4949529	0.0022178	0.0021106	-0.0286888	0.0000282	0.0016890
0.6489352	0.0023946	0.0022795	0.0321455	0.0000311	0.0067175
0.8019194	0.0023542	0.0022410	0.1124831	0.0000305	0.0132949
0.9439058	0.0013649	0.0012993	0.2881465	0.0000143	0.0204042
1.0978938	0.0045598	0.0043369	0.6191529	0.0000064	0.0280593
1.2498750	-0.0008042	-0.0007548	0.8739773	-0.0000211	0.0358074
1.4048594	0.0007902	0.0007523	1.2224644	0.0000049	0.0426593
1.5484551	0.0004702	0.0000448	1.6232664	-0.0000072	0.0500198
1.6978320	-0.0013988	-0.0013316	2.0455809	-0.0000308	0.0571921
1.8528146	-0.0007325	-0.0007161	2.4507816	-0.0000203	0.0633702
1.9938006	-0.0032056	-0.0030515	2.8598676	-0.0000603	0.0708402
2.1457853	-0.0033451	-0.0031843	3.2473726	-0.0000626	0.0779057
2.3007698	-0.0033574	-0.0031963	3.6373549	-0.0000628	0.0849588
2.4537543	-0.0040045	-0.0038120	4.0142016	-0.0000734	0.0910931
2.5937404	-0.0042447	-0.0042117	4.3587721	-0.0000802	0.0986172
2.7497248	-0.0048242	-0.0045922	4.6321814	-0.0000868	0.1052689
2.9017103	-0.0051093	-0.0048651	4.8708410	-0.0000914	0.1117163
3.0436954	-0.0051899	-0.0049385	5.0787819	-0.0000927	0.1189232
3.1976800	-0.0048908	-0.0046558	5.3078354	-0.0000879	0.1258753
3.3496656	-0.0044139	-0.0042017	5.5385574	-0.0000801	0.1329607
3.5046494	-0.0040515	-0.0038567	5.7931283	-0.0000741	0.1401293
3.6456350	-0.0038654	-0.0037752	6.0605064	-0.0000727	0.1482939
3.7976203	-0.0036907	-0.0035133	6.3657164	-0.0000683	0.1560093
3.9526047	-0.0029265	-0.0027858	6.6778459	-0.0000558	0.1642867
4.0935907	-0.0017164	-0.0016338	7.0845670	-0.0000360	0.1723062
4.2465736	-0.0003563	-0.0003392	7.3437974	-0.0000138	0.1802089
4.4005590	0.0013387	0.0012743	7.6668368	0.0000139	0.1886595
4.5535452	0.0024437	0.0023262	7.9938385	0.0000319	0.1966256
4.6945304	0.0033253	0.0031723	8.3806939	0.0000464	0.2049399
4.8485103	0.0047203	0.0044930	8.7752402	0.0000691	0.2144974
5.0014995	0.0066778	0.0062900	9.1653450	0.0000999	0.2239347
5.1554842	0.0083580	0.0079560	9.4993268	0.0001285	0.2316238
5.2964701	0.0104598	0.0099531	9.8055264	0.0001628	0.2391947
5.4494547	0.0067910	0.0064644	10.1316354	0.0001029	0.2469568
5.6034398	0.0004063	0.0004854	10.4368538	0.0000074	0.2541513
5.7444253	-0.0001343	-0.0001278	10.7648580	-0.0000102	0.2607052
5.8974103	-0.0002012	-0.0001916	11.0747430	-0.0000113	0.2698046
6.0513944	0.0011493	0.0010613	11.3270242	0.0000102	0.2801374
6.2043796	0.0021708	0.0019201	11.5249635	0.0000250	0.2888964
6.3453652	0.0033019	0.0031432	11.7579408	0.0000459	0.2977316
6.4933507	0.0041543	0.0039546	12.0447843	0.0000599	0.3084005
6.6523349	0.0058669	0.0055848	12.3827571	0.0000878	0.3188015
6.7932066	0.0078447	0.0074674	12.6629457	0.0001201	0.3215131
6.9473052	0.0098275	0.0093549	12.8993384	0.0001525	0.3402251
7.1002898	0.0109205	0.0103954	13.1638747	0.0001704	0.3528898
7.2542743	0.0128901	0.0122702	13.3726798	0.0002025	0.3620232
7.3952603	0.0153760	0.0129221	13.6788104	0.0002137	0.3712827
7.5482449	0.0138971	0.0132288	14.0188454	0.0002190	0.3817195
7.7022295	0.0145895	0.0138879	14.3193584	0.0002303	0.3868616
7.8432154	0.0163848	0.0155965	14.5312973	0.0002596	0.3969405
7.9962008	0.0191408	0.0182203	14.7298709	0.0003046	0.4085193
8.1501851	0.0202194	0.0192470	14.8809681	0.0003222	0.4159854

Figure 23. Typical final data recorded by the tensometer program.

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) upon reaching the stop time of 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.

5. Aborting during a test in-progress

There are several reasons a user may wish to stop an experiment that has already been started in LabVIEW. For example, the user may stop a test if the thermocouple is mistakenly not inserted in the sample, the NIR instrument has not been warmed up or the experimental setup may be incomplete. In such cases, the user should abort the test as soon as possible and before the curing light is illuminated. For cases in which the thermocouple is not inserted in the sample, the user does not need to re-do the sample preparation (section 1) and data collection (section 2) procedures before starting the test again; however, if the NIR instrument was not warmed up or the curing light was improperly mounted, the user should repeat the sample preparation and data collection steps prior to starting the test.

The user may abort a test in-progress by clicking the ‘Stop’ button in the main program (Figure 15). The user may edit LabVIEW test settings, if desired (see Step 4 of data collection). Next, click on the ‘run’ (red arrow) button in the main LabVIEW program window to re-set the controls in place. If the user already correctly captured the NIR initiation data prior to stopping the test, the user may click the ‘Skip’ button to skip the NIR (background, reference and spectrum) collection since it was already saved; else the user should click ‘NIR Initiation’ (see Step 6 of data collection) and repeat the initiation. Next, the user may re-start the test by clicking the ‘Start’ button. A new window prompt may appear warning the user that an existing data file will be overwritten. Click ‘Ok’ to overwrite the existing file.

Note that if the user aborts a test and closes the LabVIEW windows, the user must restart all the procedures from the beginning as all the ‘NIR Initiation’ data would have been lost from memory when the user exited the main program.

References

1. Chiang MYM, Giuseppetti AAM, Qian J, Dunkers JP, Antonucci JP, Schumacher GE, Lin-Gibson S. Analysis of a cantilever-beam based instrument for evaluating the development of polymerization stresses. *Dent Mater* 2011; 27: 899-905.
2. Wang Z, Landis F, Giuseppetti AA, Lin-Gibson S, Chiang MYM. Simultaneous measurement of polymerization stress and curing kinetics for photo-polymerized composites with high filler contents. *Dent Mater* 2014; 30: 1316-24.

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Appendix

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

(2) 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

(3) 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