Fast Oscillation Rheological Data Analysis for Real Time UV Cure Profiling and Shrinkage Determination of Developing Network Systems

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Rheology is the branch of science dealing with the flow and deformation of materials. Rheological instrumentation and rheological measurements have become essential tools in the analytical laboratories for characterizing component materials and final products, monitoring process conditions, as well as predicting product performance and consumer acceptance.

Rheologically speaking, Developing Network Systems (DNS) can range from low-viscosity radiation curable monomers, to more viscous two-component and thermally curable fluids and gels, up to hard, vitrified materials. A knowledge of the rheological and mechanical properties of these varied systems is important in the design and optimization of flow processes for production and quality control, in predicting storage and stability conditions, and in understanding and designing the required material mechanical properties.

Rheological behavior is directly associated with performance qualities such as comfort in the case of contact lenses, cure time in the case of fiber optic coatings and inks, and ultimate mechanical strength in the case of structural polymers.

Today, rheological instrumentation and rheometry are accepted techniques to more fully characterize, understand, and control the production and use of DNS materials. How a particular chemical structure is studied or analyzed, the techniques and instrumentation involved, and how these may be used or modified to solve a problem are paramount in understanding the material-structure-processing relationships.

Importance of acceptable rheology

In the case of photo-initiated DNS materials, the time-temperature-intensity transformation profile (TTIT) is the controlling rheological parameter. Following the work by Gillham and Enns in developing the use of the time-temperature-transition (TTT) diagrams, the TTIT profile accounts for photo initiated reactions, and like TTT is analogous to the phase diagrams used by metallurgists. The TTIT diagram is used to track the effect of temperature, time, and intensity on the physical state of a DNS material. Understanding and predicting the kinetics of these materials is of practical interest both in the manufacturing process and in end-product performance and reliability.

Although there have been many studies on kinetics of DNS materials, most have focused on the method of calorimetry, such as differential scanning (DSC) or differential thermal analysis (DTA). In those studies, the definition of the state of cure is not directly correlated to the physical, mechanical, or rheological properties of the material. Conversely, kinetic methods from rheometry are able to predict properties, such as viscosity and dynamic modulus, which are used to determine manufacturing operations and end-product performance of DNS materials.

The kinetics are determined from time dependent dynamic mechanical response using classical network elasticity theory to relate the measured viscoelastic properties to gelation and vitrification as a function of time, temperature, intensity, etc. DNS reactions can be classified into those that involve the loss of one molecular species, those that join “mers” together without change in the repeat structure, those that join intermediate molecular weight polymers together (crosslinking) and condensation reactions.

Rheological characterization of fast cure DNS materials requires several unique instrument capabilities, 1) data collection rates in excess of 10 sample data points/s, 2) adjustment for sample volume changes during gelation, 3) wide torque, angular displacement, and temperature ranges, and 4) ability to follow samples starting out as low viscosity liquids and proceeding to hard solids.

Rheological instrumentation

In principle, the curing process can easily be followed by using dynamic mechanical rheological measurements, as the build-up of a three-dimensional network is reflected in the change of viscoelastic properties. Today, rheological instrumentation is considered a required analytical tool by scientists and is used on a daily basis. These research grade instruments are Windows™-based, and measurements are made quickly and easily with the use of straightforward, user friendly software. The operator simply loads the sample into the instrument and selects the appropriate experiment, and the instrument does the rest.

DNS’s can be single component or complex mixtures of different materials where individual components are mixed together to produce a desired reaction profile, and/or finished product. Many times, they are not homogeneous, and the properties vary throughout the sample. Traditionally, single point viscosity tests have been performed using empirical techniques. These simple viscosity experiments compress the complex viscoelastic response of a sample into a single parameter, and are not adequate in characterizing and/or providing insight into the TTIT of DNS materials. The materials in use today are slated for high performance applications, and, as a result, the cost for these materials is high. Detailed knowledge, and an objective, reproducible, multi-point measurement, capable of decomposing the rheological behavior into individual components is necessary.

The STRESSTECH HR Rheometer equipped with optional UV Cell and Honle light source is shown in Figure 1. The rheometer and integrated light source allow for user selectable illumination and exposure time and intensity. In addition the environment around the sample and temperature can be controlled.

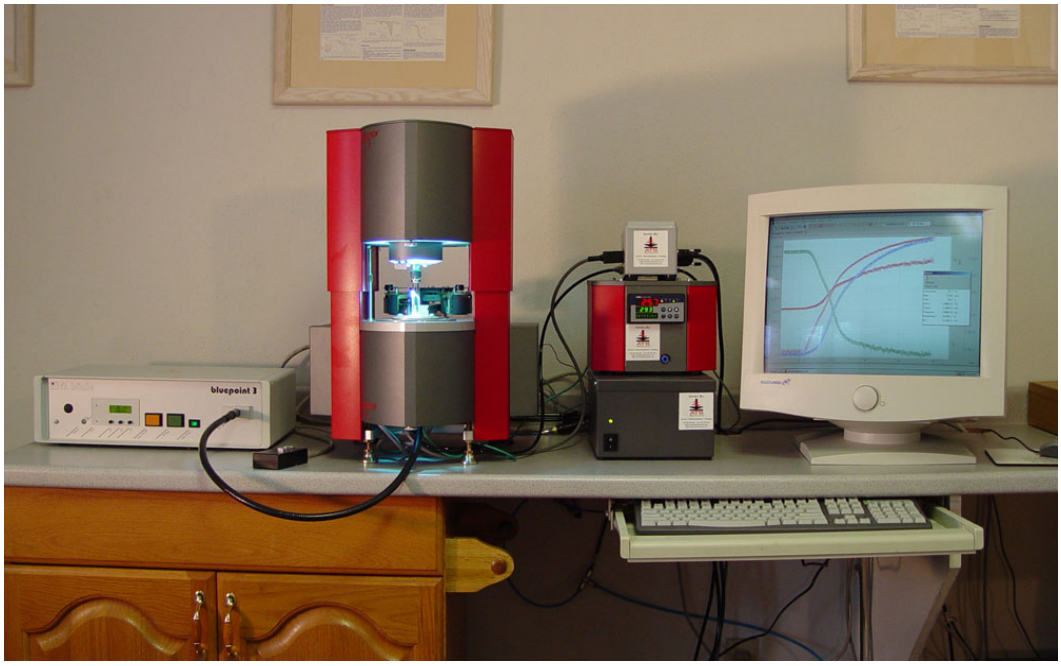

Figure 1

Fast Oscillation Data Analysis

Historically, rheological oscillation data acquisition consisted of sampling one or more periods and then deriving the real and complex components of the sample response from the measured waves utilizing an FFT. The minimum requirement of a single complete wave cycle has limited the utility of dynamic oscillation to capture very fast changes in material structure such as those that are encountered in UV curing, where the sample may change from a low viscosity liquid to a solid in a few seconds. The fastest theoretical data rate in samples/s (minimum time for each data point) would be equal to the frequency in Hz. For many DNS materials, especially radiation curable DNSs where the events of interest occur within 2 s of illumination, this data collection rate is too slow to capture the TTIT transient cure profile.

Conventional Oscillation

Data Sampling

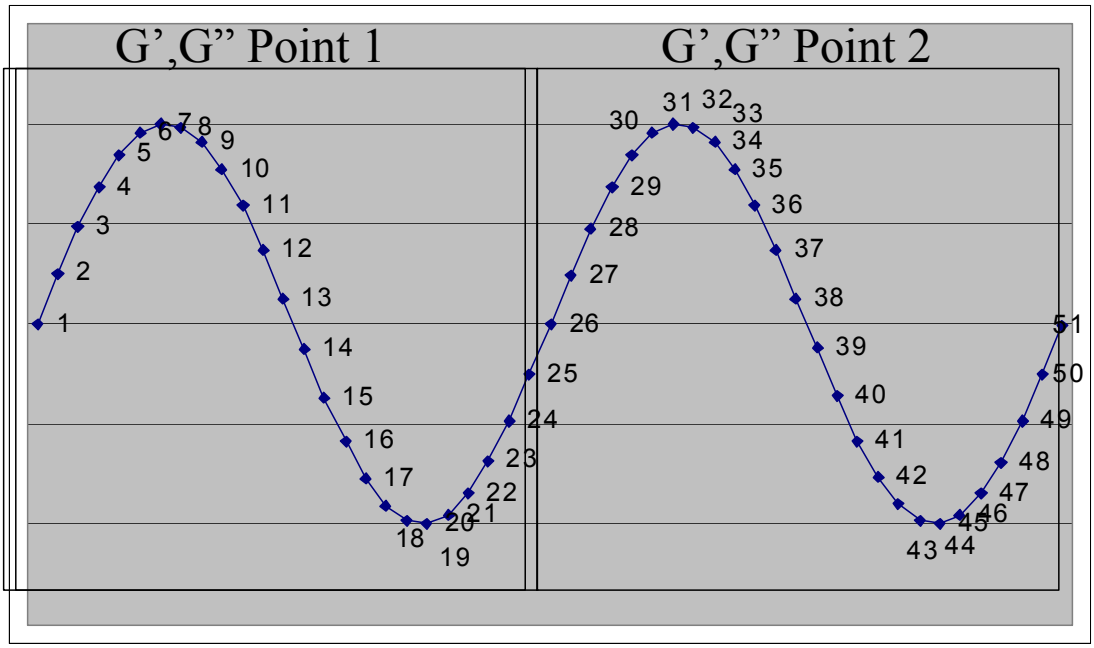

Figure 2

Figure 2 shows a conventional oscillation data sampling sequence for a time sweep at 1.0 Hz (1 cycle/s). Points 1-25 will be acquired in 1 s from the start of the experiment and then processed to provide the first data point. Points 26-50 will be acquired and processed to provide the second data point, etc.

- Points 1-25 are sent to the CPU for FFT calculation requiring ~0.1s
- The actual FFT calculation takes between 1-4 s (actual time depends on number of points collected, 128 to 2048)
- The time between each data point result will be from 2-5 s
- This data rate is exclusive of any other delay times, multiple iterations employed to reach a target strain for iterative strain control, or auto-ranging

In recent years, new techniques have been derived to obtain dynamic moduli (or compliance) using 1/4 or 1/2 wave analysis, with the benefit of faster data acquisition, albeit at some compromise in phase angle resolution. These partial wave techniques can improve the data rate by a factor of 2-4, but still suffer from the limitations listed above. These techniques still do not provide the data sampling rate adequate for capturing the transient cure profile for rapid DNS materials. A new technique, called Fast Oscillation, has been developed for data

acquisition that enables the user to acquire oscillation data at intervals as small as 1/100th of a period, with no loss in phase resolution.

The Fast Oscillation program is used to measure rapid, transient changes in a material. Based on the oscillation program, it works under the same principle where a sinusoidally varying forcing function is applied to the sample and the equally varying sample response is measured. Dynamic Oscillatory data at constant frequency are collected as a single continuous stream of waves, then analyzed via FFT using a moving average (Figure 3). G' and G" are determined at the raw sampling rate of the analog wave, instead of the period of the oscillation. The measured values are evaluated by one of several sampling methods selected by the user. The number of measurement points to be measured and presented can be set by the user, allowing data collection rates greater than 100 points/s.

Fast Oscillation

Data Sampling

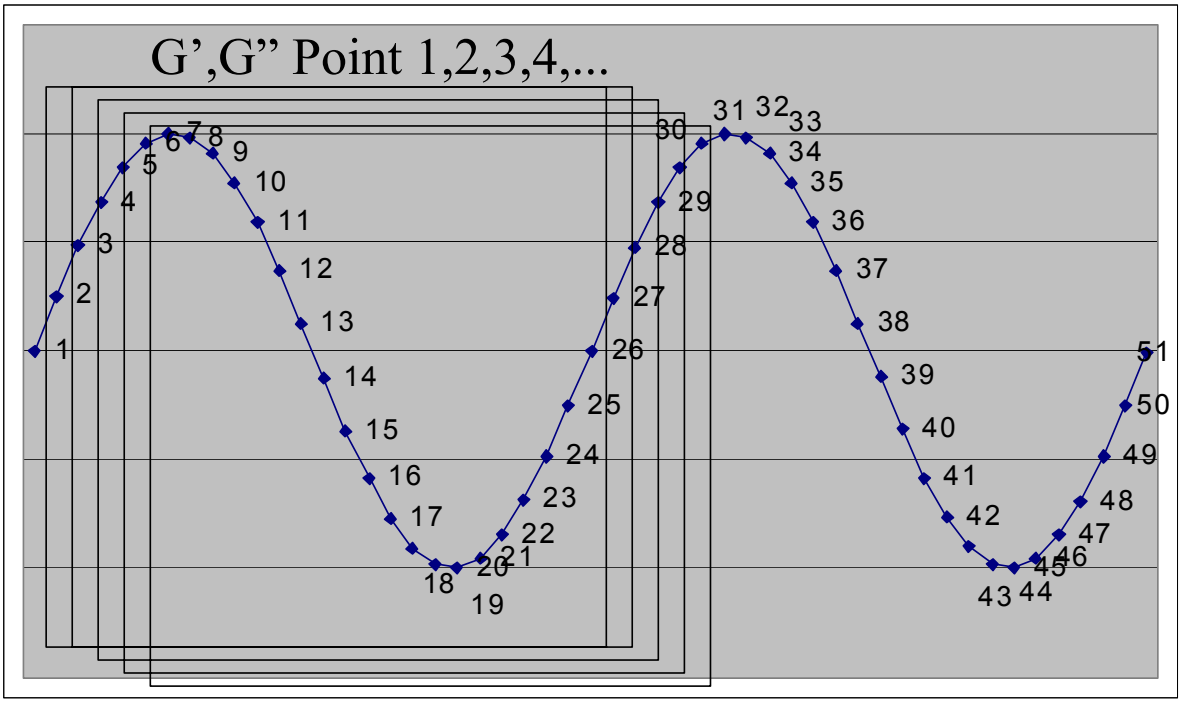

Figure 3

Figure 3 shows a Fast Oscillation data sampling sequence for a time sweep at 1.0 Hz (1 cycle/s).

- Points 1-25 acquired in 1.0 s and sent to FFT to generate 1st data point (same as standard oscillation program)
- Points 2-26 acquired in an additional 0.04 s and sent to FFT to generate 2nd data point
- Points 3-27 acquired in an additional 0.08 s and sent to FFT to generate 3rd data point
- The time between data points is 1/25=0.040s
- The data acquisition rate is 25 times faster than standard oscillation program run at the same frequency

The Fast Oscillation Program also includes the ability to control the shutter of a remote light source. The Relay Setting dialog box allows the user to set the intervals during which the light source shutter is turned on and off. In addition, the user can select to employ auto-tension to account for sample consolidation as a result of crosslinking.

Typical Fast Cure Profile of DNS Material

The cure of DNS materials typically results in shrinkage of 10-15%. If the measurements are made with the gap at a constant setting, the shrinkage of the materials will result in large internal stresses during the cure after gelation. ATS RheoSystems/REOLOGICA Instruments has developed the rheometer, STRESSTECH HR, and software, RheoExplorer V5, to handle this by allowing the operator to change from a controlled gap setting mode to auto tension mode (in which the axial normal force is controlled) at a user selectable point or event. For measurements in the liquid state, the gap setting must be set at a constant value, but by the time the gel point is reached the shear modulus has increased sufficiently for the sample to maintain its shape. Although shrinkage occurs throughout the chemical reaction, internal stresses will develop only after gelation occurs. Utilizing the “Expert Condition” dialog selection, as soon as the gel point is reached (i.e., tan delta =1), the instrument changes to auto-tension mode and maintains the normal force at zero during the remainder of the cure cycle. The shrinkage can be monitored quantitatively using the gap measurements.

An example of an experiment run under these conditions is shown in Figure 4. A typical fiber optic primary coating with photoinitiater is cured photochemically between the 25-mm diameter plates of the rheometer equipped with the UV cell. Initially the gap is set at 0.2 mm. The dynamic shear moduli (G’ and G”) rise rapidly after the shutter is opened, while tan delta (=G”/G’) drops from infinity (G’=0 in the initial liquid state). When tan delta drops below 1, the auto-tension mode is employed, and the reduction in the gap can be monitored during the remainder of the cure.

Without the adjustment to reduce the internal stresses, the measurement of the rheological properties in the solid state may be compromised by artifacts due to the delamination of the sample from the plate, or the formation of voids in the sample.

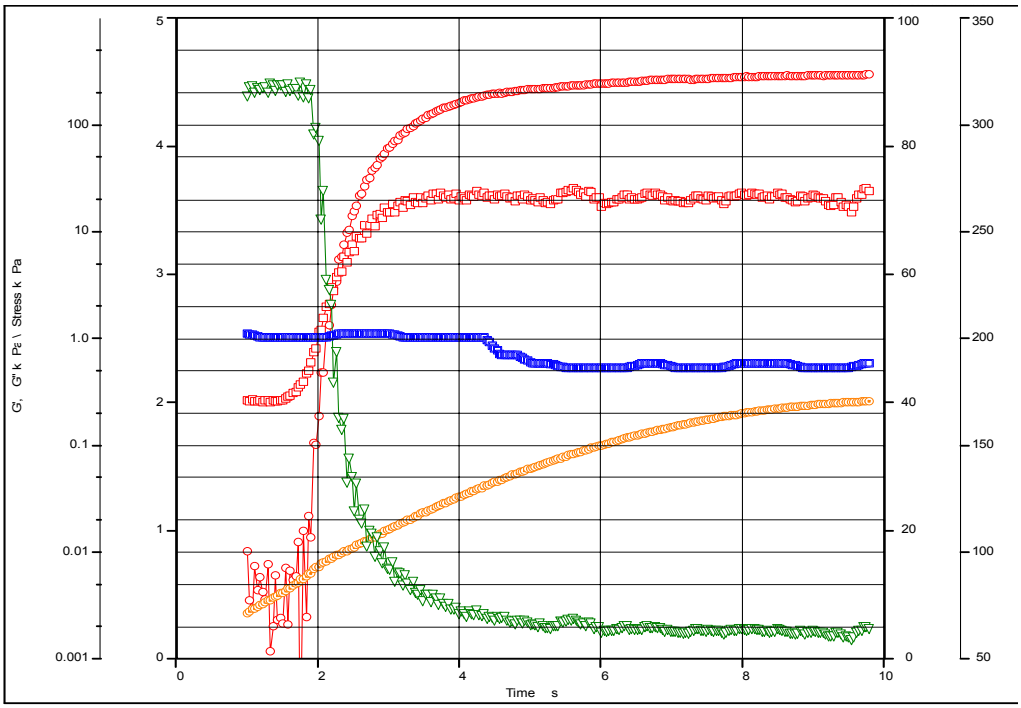

Figure 4

An example of the Expert Condition dialog test parameter setup is shown in Figure 5. The user can select the point at which to start controlling the applied Normal Force on the sample, and, in addition, the point to terminate the experiment once the sample achieves full cure based on its measured viscoelastic properties.

Measurement Control Dialog box

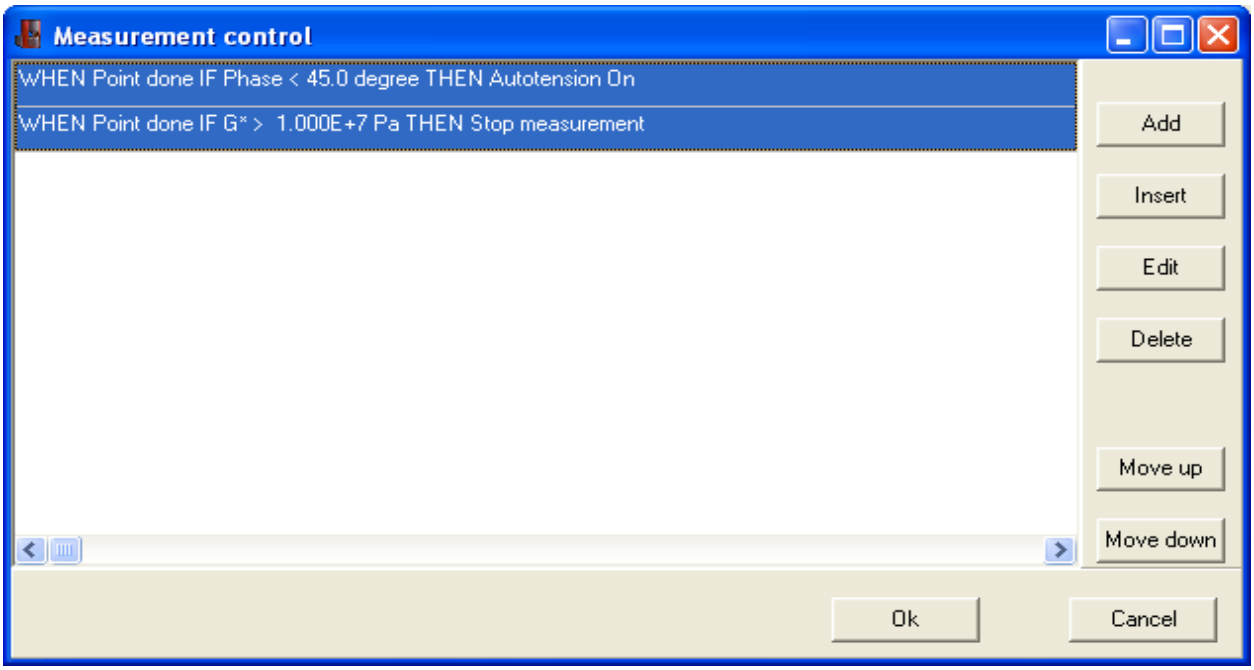

Figure 5

Another important requirement for fast curing system is the ability to maintain the appropriate strain throughout the cure profile. The rheometer software has the ability to model the cure profile by employing either a constant, sigmodial, or polynomial stress coefficient (Figure 6). This feature is essential in measuring materials that undergo several orders of magnitude change in modulus during cure. By utilizing these different stress profiles, the sample can be tracked from a low viscosity fluid to hard vitrified solid regardless of its beginning, intermediate, and ending viscosity/modulus values.

Stress Waveform

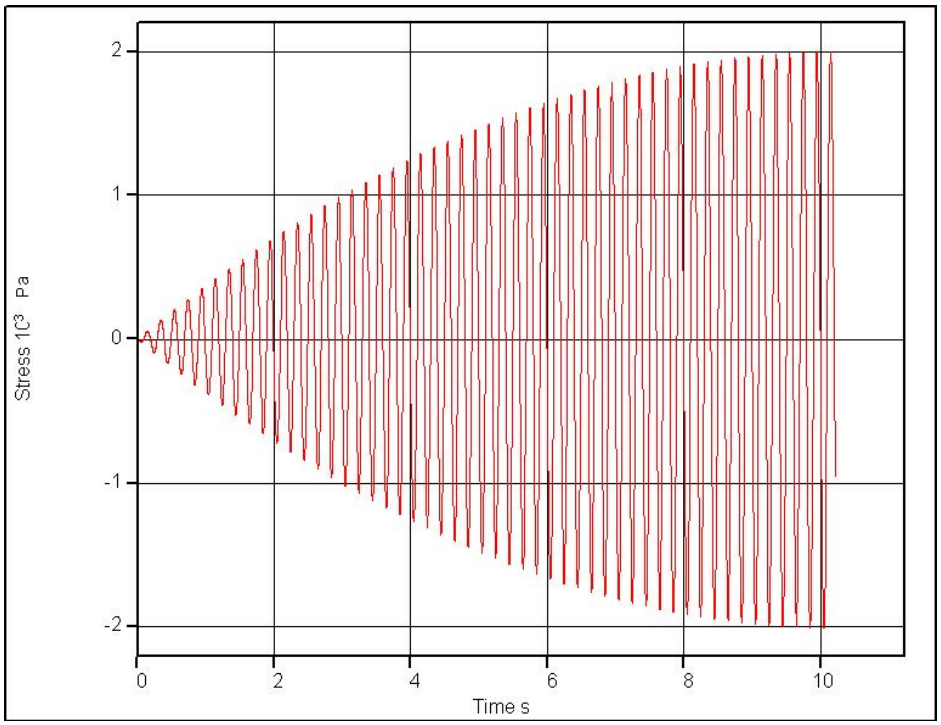

Figure 6

Conclusion

This article reviews the important rheological characteristics for real time light curable materials and presents results generated with a STRESSTECH HR Rheometer on UV curable fiber optic coatings. In addition, a detailed interpretation of data and correlation of the rheological response with the physical/chemical properties of different DNS materials has been presented. The rheological characterization of DNS materials provides important information for engineers and scientists to improve and optimize their products and manufacturing processes. Today, most researchers and manufacturers count on rheological measurements to develop customer favored products with a competitive edge in the marketplace. A reliable research level rheometer and a thorough understanding of rheological measurements is now a necessity for success in today's marketplace.

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