APN003

Benefit of Fast Data Acquisition during Rheological Measurements

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ABSTRACT

Rheological measurements made in oscillation in general operate on strong signals, both stress and strain. With increasing complexity of materials, the need exists to cover wide ranges in sample modulus (and hence stress and strain) during a single measurement. For dynamic ranges better than 10^6, random noise has to be eliminated and systematic errors corrected in order to insure accurate results. Fast data acquisition combined with a flexible correlation technique is required to improve the low end performance of an oscillatory rheometer. The harmonic analysis of large strain amplitude oscillation tests is becoming a very useful technique to characterize subtle differences in materials' structure. A fast data acquisition is a must for the determination of magnitude and phase of the higher harmonic response in a non linear oscillation test. UV curable adhesives and coatings change from a low viscosity fluid to an elastic solid within seconds. Fast data sampling associated with a flexible window correlation method can provide up to 100 data points per second – thus allowing an accurate monitoring of rapid changing processes.

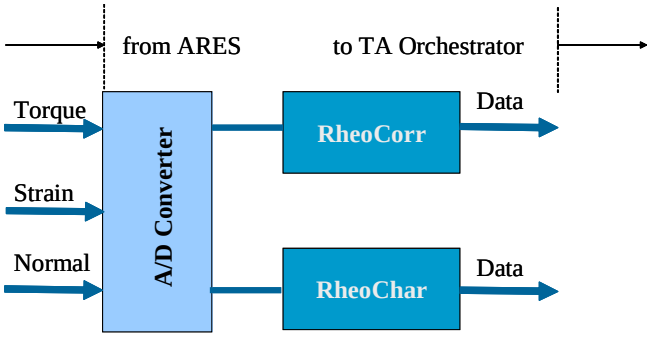

Figure 1: External fast data acquisition option

INTRODUCTION

Fast data sampling is not a requirement for standard rheological testing because the rheometer inertia limits the measurement to a range above 0.01s in transient or below 100Hz in oscillation. The measured signals usually are strong and bigger than random noise. The advanced rheological characterization of complex fluids or rapidly changing material systems however requires faster data acquisition to increase the dynamic range of the torque sensor or to be able to monitor rapid rheological changes. In the following the need for rapid data acquisition in oscillation is demonstrated to: a) reduce random noise and thus increasing the dynamic range of the rheometer, b) monitor the rheological changes of UV curable adhesives and c) do higher harmonic analysis in the non-linear oscillation regime.

EXPERIMENTAL

The measurement of dynamic mechanical properties from the transient stress and strain signals involves the calculation of the magnitude of each of these sinusoidal signals and their respective phase. In commercial rheometers, the techniques used are either a discrete Fourier transform or a cross correlation algorithm. In the case of the cross correlation, the incoming stress and strain signals are correlated against two reference sine waves of the same frequency that are shifted in phase by 90° from each other [1]. For the determination of the higher harmonics, the reference waves operate at the desired multiple of the fundamental frequency e.g. the third multiple for the third harmonic. The correlation algorithm provides excellent noise rejection, particularly if the results are integrated

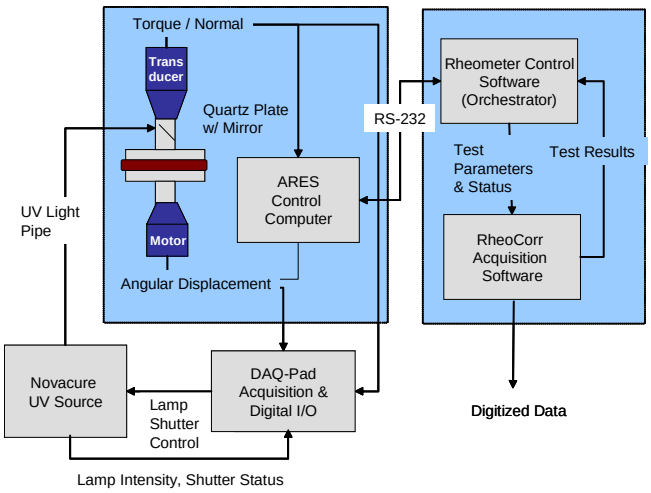

Figure 2: Experimental setup with fast data acquisition and UV curing option

over many data points. The ARES instrument computer uses two dedicated A/D converters and correlates on a fixed number of 2048 raw data points within the time of minimum one cycle below 2 rad/s. For fast data acquisition the ARES rheometer hardware has been enhanced with an external A/D converter with significantly higher sampling rate, a separate correlator and special software to interface the TAOrchestrator software which automatically sends the data stream to the instrument data presentation software (Figure 1). The signals of strain and stress are available via BNC connectors at the back of the instrument and are digitized using a National Instruments analog to digital converter (PCI-MIO-16XE) with 16 bits of resolution and a maximum sampling rate of 100 kS/s for one channel. The signals are scaled to +/- 5 V full scale, which corresponds to the full scale of the torque transducer and to 0.5 radians of angular displacement for the motor. The A/D converter can be manually rescaled f.ex. 0.5 or 0.05 V full scale, to increase the resolution when weak signals are to be expected. The correlator module, "RheoCorr" interfaces the data acquisition system with the instrument control software – thus enabling TAOrchestrator to control the external hardware (remote control), send over the appropriate scaling constants and to receive the calsulated dynamic mechanical data. The correlator module has the flexibility to allow independent setting of the number of correlation cycles (minimum 0.5 cycles), the number of data points per cycle (maximum is limited by the sampling rate of the A/D converter) and the correlation frequency i.e. the interval between correlation operations. For testing UV curing materials, the Novacure 2100 UV source can interface with the external DAQ hardware (Figure 2). Lamp shutter and UV intensity are controlled from the operation software during the test. Special upper quartz plates are used to illuminate the sample with the UV radiation. A flexible glass fiber light pipe with 5mm cross section conducts the UV light near the UV test fixture. The radiation intensity is homogeneously redistributed over an area of 20mm of diameter with a collimator and then reflected onto the upper quartz plate by a mirror build into the test fixture stem.

RESULTS AND DISCUSSIONS

Sensitivity and data correlation

A high data acquisition rate and optimized data handling significantly enhances the dynamic range of the torque signal i.e. increases the sensitivity of the torque transducer. The sensitivity here is defined as the ratio of the detected signal to noise [2]. The noise is the uncertainty of the measured quantity and is given by the relative standard deviation of the modulus and the phase. In order to increase the

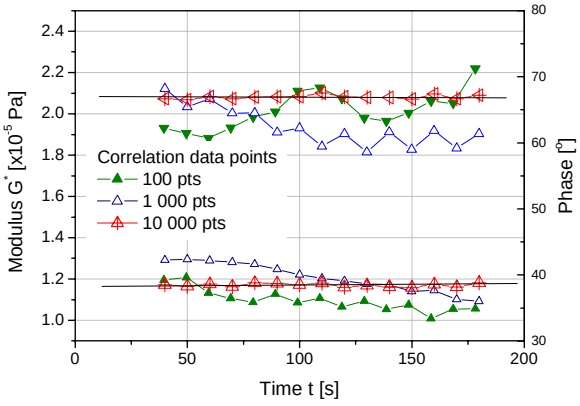

Figure 3: Variation of the phase and modulus with increasing sampling rate

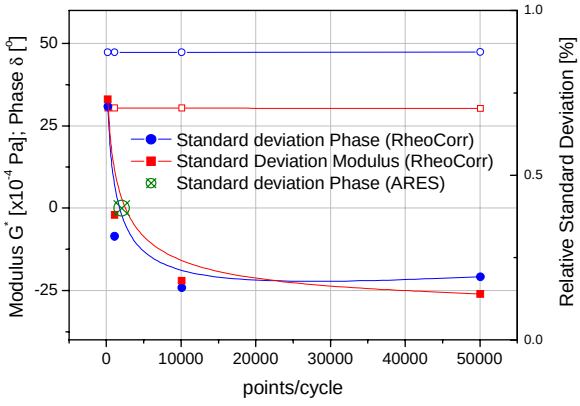

Figure 4: Error in phase and modulus with increasing sampling rate

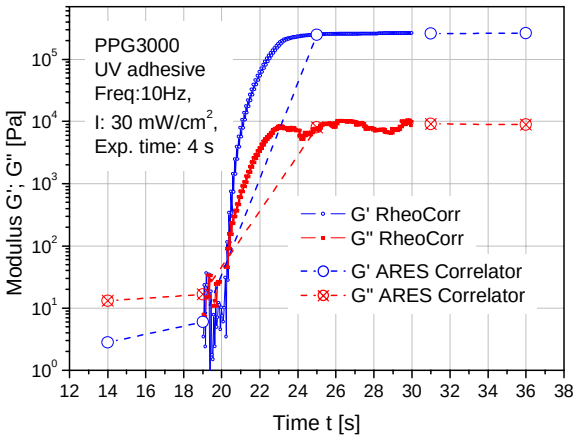

Figure 5: Trace of G' and G" during curing, monitored with RheCorr and the ARES correlator

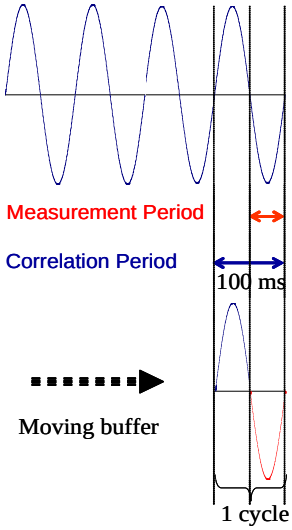

Figure 6: Under-sampled data correlation technique

S/N ratio, the results are averaged over an increasing number of data points. The sensitivity grows in the case of random noise only, with the square root of the measured transient data points $S/N \sim n^{1/2}$ [3]. The accuracy of modulus and the phase angle have been analyzed as a function of the number of correlation cycles and data points per cycle in figure 3. At low applied strain the raw signals show significant scatter, which leads to large variations in the calculated modulus or phase if only few data points are sampled. The figure 4 shows the error in phase and modulus, which decreases with increasing number of data points per cycle, here for a PDMS sample tested at 0.1 Hz and 0.5% strain (0.8mrad angular displacement). Little improvement can be seen after 10000 data points. This means, that systematic errors are contributing to the noise also. Wilhelm and al. used an over-sampling method [2] to reduce the large data sets for the Fourier transformation after the data acquisition. Since the cross correlation technique can easily handle large data sets (300 000 data points for the example in figure 3) over-sampling thus is not necessary to improve accuracy.

Monitoring the changes of UV curing adhesives

UV curing materials are the choice, if fast setting of an adhesive or a coating is required. Since these systems cure within seconds, fast data acquisition is necessary to monitor the rheological change in a rheometer. Figure 5 shows the cure behavior of an UV curing adhesive. At a probing frequency of 10Hz the ARES correlator uses several cycles and collects one data point every 5 seconds. The external correlator "RheoCorr" combined with the fast data acquisition is able to provide a data point every 50 ms i.e. 20 points per second - thus monitoring the cure much closer with no loss of accuracy (The results of the external and the standard ARES correlator virtually superpose in Figure 5). In order to generate a data point every 50 ms and still be able to correlate over one full cycle, an under-sampling technique is used (Figure 6). In this case the digitized analog signal data of the last 100 ms (which equals the time of one cycle at 10 Hz) are kept in a buffer and every 50 ms the correlation of the buffer data provides a new value for the modulus. Under these experimental conditions, 50% of the raw data in the buffer is old every time a new modulus value is determined and the modulus is an average value over the correlation period. The parameter controlling the resolution in time during a cure is the time necessary to fill or renew the buffer. The buffer time is directly related to the test frequency. Theoretically, a quarter of a cycle is sufficient to perform a correlation, "RheCorr" does

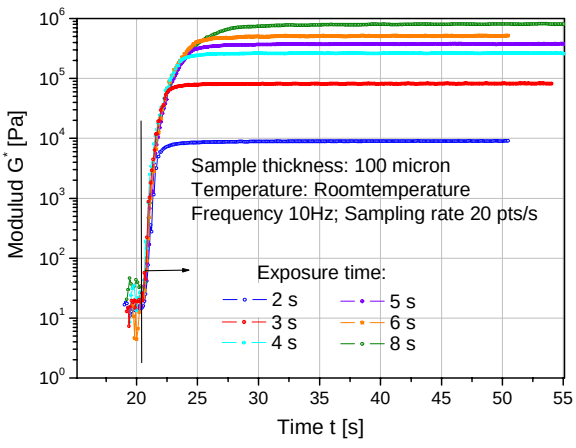

Figure 7: Curing of a UV curing adhesive as a function of the UV exposure time (I=30mW/cm²)

not allow less then half a cycle in order to eliminate large correlation errors. This means that at a probing frequency of 10 Hz, the minimum buffer length is 50 ms (1/4 cycle). However in order to improve the overall accuracy, 1cycle and higher correlation is preferred. The under sampling technique permits under these conditions to hold on to the 50 ms correlation interval. Figure 7 exhibits a series of cure traces of the same adhesive as a function of the UV exposure time. The modulus reaches its maximum value after about 8 seconds exposure time for an intensity of 30 mW/cm^2. The UV exposure is controlled by the rheometer and the shutter can be switched on and off while the experiment is running.

Determination of the higher harmonic response

In oscillation data analysis is usually done in the linear range only. However recent investigations by Wilhelm [4] show that the higher harmonic content in the non-linear response provides additional information, which can be related to the material's structure as well as to material performance. The highest harmonic frequency available is the Nyquist frequency, which is $\nu_{max}=1/(2t_s)$ with t_s being the inverse of the sampling rate. In order to increase the spectral resolution, i.e. the highest measurable frequency as well as to increase the sensitivity, the sampling rate needs to be increased. The fast data acquisition option provides this feature. The 3rd, 5th and any higher harmonic frequency response are obtained by correlating the measured signal from an oscillation test with a reference signal at the desired harmonic frequency. Figure 8 shows the raw signals of the torque as the amplitude of a sinusoidal strain is increased from 1 to 20% for a cosmetic emulsion. Whereas at 1% strain, the torque response shows to be predominately sinusoidal, does the torque response at higher applied strain follow an non-symmetric periodic function. This behavior is a result of the uneven higher harmonic contributions. The final result is reported as the magnitude of the torque signal obtained from the 3rd harmonic divided by the fundamental torque amplitude I(3ω)/I(ω). Figure 9 shows the evolution of this intensity ratio of the 3rd harmonic as a function of the applied strain for the same emulsion. For reference, the storage and loss modulus G' and G" are shown. The higher harmonic contributions become significant as the modulus decreases and the material behaves non-linear above 1% strain.

CONCLUSIONS

Fast data acquisition enhances the oscillation testing capabilities of rotational rheometers in three areas: - the low end sensitivity by reducing random noise of the measured torque of displacement signals, - the monitoring of fast changing process like UV curing systems and – the accurate measurement of higher harmonic contributions in the non linear viscoelastic range.

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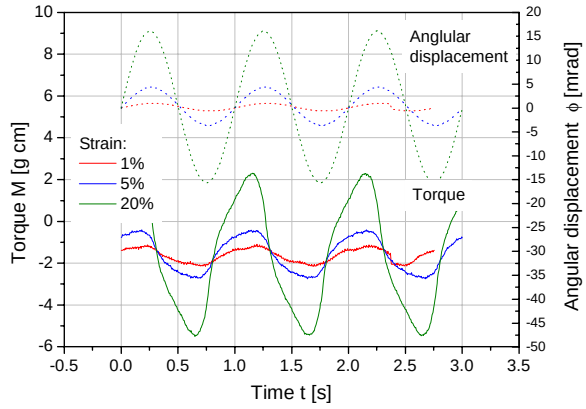

Figure 8: Curing of a UV curing adhesive as a function of the UV exposure time (I=500mW)

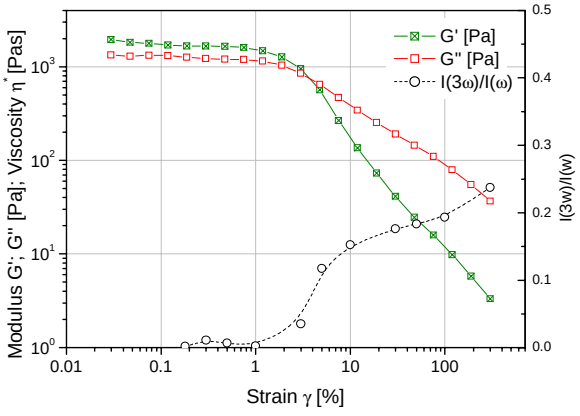

Figure 9: G', G", 3rd harmonic torque ratio vs. strain for an emulsion